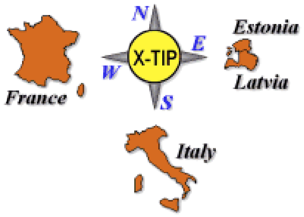
STRP 505634-1 X-TIP



X-TIP

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

Specific Targeted Research Project (STRP)
supported by European Commission 6th Framework Programme

Thematic Priority **NMP**

Publishable Final Activity Report

Period covered: from **1/03/2004** to **28/02/2007**

Date of preparation: **06/2007**
Revision 3

Start date of project: **1/03/2004**

Duration: **36 Month**

Project coordinator name: **F. Comin**
Project coordinator organization name: **ESRF**

Contents

Publishable Executive summary

I Objectives

The perspectives of nanotechnology in tailoring the physical-chemical characteristics of nano-objects are linked to our knowledge and control of their shape. Any characterization technique has then to be linked with a morphological knowledge of the sample. In 2004, when the X-Tip project started, it was already possible, in many facilities of the world, to focus the beam on spots of about 100 nm, but there was no possibility of *in situ* visualizing samples with thesedimensions, making impossible the link between spectroscopic characteristics and size. The only way out was a cumbersome procedure of mapping via SEM or other ex-situ microscopies to be transferred to the X-ray microscope alignment system.

The objectives set for the X-Tip project were then quite wide: on one side we wanted to give an answer to the need of navigating over the surface under examination and provide the possibility of mechanical intervene to modify it (moving and aligning dots, applying pressure), and on the other side we wanted to explore all the possibilities to utilize the tip itself as a detector, in such a way to leave the definition of the lateral resolution of the measurement to the tip geometry and *not* to the spot dimensions.

The exploratory character of the project was linked to the emerging needs of nano-characterization techniques and in phase with the development of Synchrotron Radiation instrumentation.

I.1 The partners and their expertise

The partners who participated in the project and their specific expertise were:

- ESRF - Grenoble: expertise in X-rays, beam stability and control, engineering and system integration.
- CNRS/CRMCN - Marseille: expertise in Scanning Probe Microscopy (SPM) developments.
- CNRS/LEPES - Grenoble: expertise in small force measurements and SPM measurements
- ISSP – Riga (Latvia): expertise in laboratory set-ups and XAS techniques
- UNITN – Trento (I): expertise in XEOL detection and XAS techniques
- UNITA – Tartu (Estonia): expertise in custom sample and tip production
- CNR/IFN Trento (I): expertise in XEOL physics of confined systems and XAS techniques
- CNR/INFM (Grenoble): expertise in X-ray surface diffraction and absorption

The listing takes into account the organizational changes which intervened after the start of the project and does not take in account two Swedish partners competent in sample preparation who have been excluded after the first round of negotiations.

I.2 WPs and the Organizational structure

The project was structured around five Work-Packages (WPs) centered around two main domains of development and with a sixth WP dedicated to management.

- WP1: Engineering of beamline and software Integration
- WP2: SNOM development
- WP3: Electron detection
- WP4: Capacitance detection
- WP5: Mechanical interaction
- WP6: Management

Geographically, a first domain of expertise and collaboration was based in Grenoble (WP1, WP3 and WP5; ESRF, CNRS/LEPES, CNR/INFM) and focused on development and integration in the beamlines of AFM instrumentation for total yield detection and force measurements.
A second domain of expertise focused on the development of SNOM probes for XEOL and capacitance measurements (WP2 and WP4) and involved CNRS/CRMCN, UNITN, CNR/IFN, ISSP and UNITA.

I.3 Structure of the report

The report consists of 8 main chapters, completed by bibliography, Annexes and workshop proceedings. The patent situation and one of the PhD thesis financed by the X-Tip project can be found in the Annex as well.

At first, the report presents the state of the art at the beginning of the project (Chapter II) and the deliverable as defined after the negotiation phase (Chapter III). Then it presents the essential elements of the developed instruments and the benefits they bring to the community. The future perspectives of use of these instruments and of their future declinations are presented as conclusions.

II Setting the scene

II.1.1 Synchrotron Radiation perspectives in the years 2003-2004

To illustrate the rationale and the evolution of the X-Tip project, the perspectives and the instrumental possibility of synchrotron radiation research at the beginning of the project, in the years 2003-2004 are presented.
In that period SR was already strongly turned towards micro-characterization of materials, both hard and soft. Every SR facility in the world had at least one beamline dedicated to microbeam and the term nanoprobe was making its way in the technical glossary of SR.

The rationale for higher and higher resolutions was coming from material scientists who wanted to explore the intrinsic properties of materials beyond its granularity, while device technologists were in quest of answers and solutions to their daily problems in the manufacturing of smaller and smaller circuitries. Biologists, of course, in their attempt to penetrate the structure and functionalities of life in all the range of scales were among the most motivated in providing the thrust for moving from micro to nano.

The potentialities of SR for answering the large variety of questions opened by this plethora of “customers” were (and still are) resting both in classic and well known properties of Synchrotron Radiation and on new functionalities that third generation facilities had the possibility to explore. Among the classic properties is the high penetration depth of X-rays that make them ideal to explore the bulk of the materials or to study in-situ their surfaces in

very confined areas (megabar Diamond Anvil Cells, electrolytic cells, fully operational fuel cells, batteries, microelectronics chips). Another classic property is the chemical sensitivity of X-ray that offers the possibility of mapping the distribution of different elements or following the chemistry of specific reactions in materials.
But new characteristics, like the coherency of the beams emitted by the last generation of SR facilities were opening new ways to explore matter: the analysis of X-ray speckles from nanocrystals could bring to the determination of their exact shape in the real space. Of the same token, pushing the technique even further, the possibility of directly determining the structure of a molecule by collecting a large amount of data from single molecules it has been shown. The demonstration of these possibilities came only recently, but the ideas were already circulating some years ago.
The X-ray Magnetic Dichroism had already shown the possibility of studying the magnetic structure of material with a lateral resolution solely limited by the later resolution of the probe.

In simple words, SR could afford to provide chemical characterization of any type of sample at a lateral resolution defined by the capability of focusing the X-ray beam. However, the pure morphological study of the sample is not really at hand.

Focusing Synchrotron Radiation.
In those years, the possibilities offered by technology and the expectations of the scientific community in the development of optical elements in the X-ray optics domain were well below the present enthusiasm. Presently, it is believed that focusing down to 1 nm is actually a matter of engineering, making the X-ray one of the most powerful characterization tool for nano-systems.

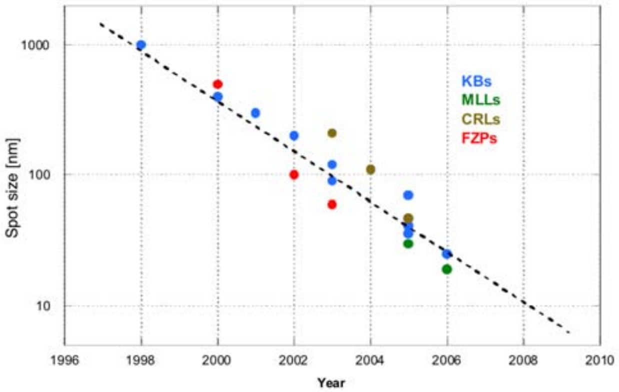


Fig. II.1 *Progresses made by X-ray optics in the last years using different focusing techniques. In 2003 a focal spot of 100 nm represented already a tremendous technical achievement, where now-a-days the most ambitious projects aim to focal spots of 1 nm for comfortably working at 5nm.*

In 2003, instead, the morphological and dynamical studies of the nanoworld were essentially dominated by Scanning Probe Microscopies (SPM: AFMs, STMs, SNOMs, etc.) even though they are essentially blind to chemical differentiation, probably the most limiting factor of these techniques.

Combining SPMs and Synchrotron radiation
It is in this general scenario that many different groups around the world thought of the interest of marrying SPM techniques with SR in order to give chemical eyes to the former and a secure grasp and lateral resolution to the latter.

Many groups around the world were caressing the idea of such a merge, but all of them judged the risk too high for embarking in such a project.
The ESRF in Grenoble was starting a serious effort to enter in the nanoworld through specific development of optical technologies like Kirkpatrick & Baez focusing mirrors, Compound Refractive Lenses (CRLs) and X-ray focusing graded multilayer structures.

Nevertheless, it has been judged important to embark with willing partners in a risky project with largely unknown difficulties (how to handle the high level of noise of Synchrotron Radiation end stations, how to avoid the interference due to X-ray disturbances, how to find a consistent way to fabricate thin fiber tips, etc.) and well known handicaps (difficulty of access beamtime for testing, modifying and testing again and again: the key element of success for a R&D project).

The integration in the project of very difficult implementations as capacitance measurements demonstrates the wide spread of directions that the project wanted to cover for a complete exploration of the possibilities offered by this merging of SPM and SR techniques.

The WP5, the mechanical interaction between tip and surfaces for modifying the structure or understanding at nano-scale processes like friction has been added in a second time in order to push the investigation of the possibilities offered by the integration of the two techniques to its limit.

III The general deliverables of the project and the negotiation

The initial target of the project was to provide a complete and self-consistent instrument which could:

- Integrate the different SPM heads: electron detection, photon detection, capacitance detection.
- Integrate all the focusing and alignment tools necessary to shape and monitor the X-ray beam.
- Integrate all the embedded software and specialized script codes for data collection.

More socio-cultural targets were added to this main deliverable list essentially aimed at accelerating the integration of the Baltic countries in the mainstream of the collaboration network (Description of work page 17 of Annex 1).

The project being essentially instrumental in its main character, it appeared sensible to insert few basic research themes as part of the program. The two Swedish partners were essentially focused in this direction.

In the negotiation phase the budget requested to complete the project has been considerably resized, raising a number of question marks on the way to reach the final result.
Considering the proposed budget cut of about 50% it was then decided to limit the extent of the demonstration activities by starting excluding two Swedish partners and trying to reshape the program without jeopardizing its exploratory and open character.
As the new proposed budget was not consistent anymore with the development of a self-consistent instrument, it was then decided to deliver simplified instruments using as much as possible the hard and soft instrumental components already present on the beamlines or developed by the partners.
The deliverables changed from a single integrated instrument to a variety of demonstration instruments which could be integrated on beamlines. This change, actually, has been quite fortunate, because experience showed that the real need in Synchrotron Radiation is not for all-in-one integrated instruments, but for diffuse type of different and flexible instruments, as it will be better explained in the following.

In conclusion the concept retained after the negotiation phase kept the essential exploratory character of the project without any cut to the number and extent of the WPs in order to explore as much as possible development directions and find the most consistent technologies to install on BLs.

In reference to the list of deliverable on chapter 7.2 of the Annex one and reported below the following comments apply:

D1, D2 and D3, refers to reports, publications, participation to conferences. A non exhaustive list of papers and meeting participation is given in Chapter X.

D4 refers to Dissemination of Achievements in other forms than conferences. Here contact with SR users, Universities (UJF, Trento, Riga), industries, distribution of leaflets (see in annex) played their role.

D5, information about current state has progressed regularly.

D6, technology transfer has been done by creating a start-up, “Small Infinity”.

D7, Competence and Expertises have been enhanced considerably and a new technology is emerging for interacting with sample under X-ray beams.

D8, SR facilities have been used by all partners

> D9, New materials were supposed to be developed by the two partners who have been excluded from the project as consequence of budget cut of about 50%.

D10, new methods and technologies (BL AFM, CD AFM) have been developed.

D11, new devices have been developed, industrialized and commercialized. Others are at level of laboratory prototype.

D12, educational activities have been done through PhD thesis, conferences.

Deliverable No	**Deliverable title**	**Delivery date**	**Nature**	**Dissemination level**
D1	**Research, Midterm, intermediate and final management reports**	6,12,18,24, 30, 36	**R**	**PU**
D2	**Publications – new knowledge**	18, 30	**R**	**PU**
D3	**Proceedings**	12, 24, 36	**R**	**PU**
D4	**Dissemination of achievements**	1-36	**O**	**PU**
D5	**Information about current state**	1-36	**O**	**PU**
D6	**Knowledge or technology transfer**	1-36	**O**	**CO**
D7	**Enhance competence and expertise**	1-36	**O**	**CO**
D8	**Use of large EU facilities**	6-36	**O**	**PU**
D9	**New materials**	12	**O**	**PU**
D10	**New method or technology**	24	**O**	**PU**
D11	**New devices or instruments**	36	**P**	**PU**
D12	**Educational activities**	1-36	**O**	**PU**

IV Structure and Functionalities of the Instruments

For all the WPs the main requirements for the instrument architecture are essentially the same:

- A modular vacuum structure that could host different heads, be mounted on BLs.
- Heads that could provide independent alignment for the probe (the tips) and the sample
- A scanner for rastering the sample under the beam and the tip
- Phase lock electronics for the control of the distance probe-sample immune from the disturbances induced by the beam.

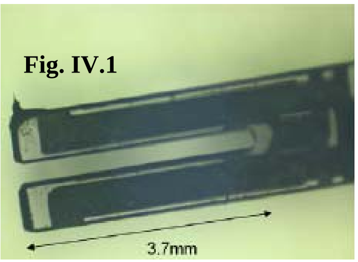


Fig IV.1 Quartz tuning fork

At the end of an initial testing period all the partners agreed on the choice of tuning forks as the tip-surface distance probe. A quartz tuning fork “probes” its distance from a surface by “feeling” the induced forces that change both its resonance frequency and the phase. Regulating these parameters, it is then possible to regulate the distance. With respect to other sensing systems this one has the advantage that it does not use detection channels other than the force, leaving all other channels (current from the tip, laser light reflections, etc.) free for other uses (see in the following).

For the positioning system, again after some trial tests, the choice has been for inertial positional systems as the one shown on the side for their small size and flexibility, low price, vacuum compatibility, acceptable stiffness and very high ratio stroke/resolution.

WP1, WP3 and WP5 chose the RHK SPM 1000 and XEOL WP chose the NT-MDT controller.

Integration on the beamline implies a number of steps. On the mechanical side the instrument has to be compatible with a number of constraints:

- Fit the tight space between the last X-ray optical element (typically 150-200 mm), the alignment microscopes and the X-ray fluorescence detectors (typically 100 mm).
- Be immune as much as possible to the high level of mechanical and electrical noise of BLs.
- Be of easy mount and dismount for maximum efficiency.
- Be provided with full remote control on all mechanical and electronic adjustments.
- Be provided with easy plug-in devices for the change of forks and tips.
- Be provided with optical windows for the first coarse alignment (>1 micron).
- Be stiff enough to keep in regulation while moving the cradle where it is mounted.
- Be provided with ports for pumping down.

On the software side integration implies that the different regulation loops which intervene in the overall control keep stable and do not interfere. Among them we mention:

- The PLL system detect the frequency of the oscillator and keep it constant
- The PID loop control the probe surface distance
- The lock-in phase detection that discriminate the good signal from the background
- The beamline control and feedback system for keeping the beam steered
- The scanner system gives the imaging capability.
- The overall scripting language for scan and acquisition

With respect to other projects which do not need Synchrotron Radiation, this one suffers of the classic difficulty of any instrumental project for SR: lack of beamtime. The value of the Synchrotron beamtime is such, that access to endstations is extremely difficult and does not permit the usual refinement of instrumentation.

IV.1.1 The probes: tips and fibers

In all scanning probes microscopies the probe has of course a central role. Its shape defines the lateral resolution, its stiffness the noise, and the stiffness of its support its resonance frequency.

One characteristic of all the SPM tips is that they are essentially good only once: they often have to be changed .

The main types of probes that have been used in this project are metallic tips for electron detection and quartz optical fiber probes for detection of optical photons emitted from the surface.

IV.1.1.1 Metallic tips

Since the beginning, metallic tips have been prepared fresh before the experiment. Etching procedures are not difficult but have to be mastered for not stressing the tip in the last seconds of etching that would result in shapes as the one figured on the left instead of the tip on the right.

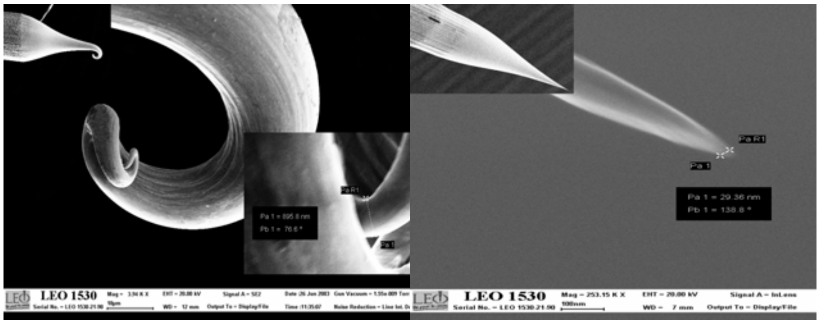


Fig. IV.2

As it will be detailed in the following, the bare metallic tips have to be covered by a thick insulating layer to prevent, at least partially, penetration of the X-rays, but, more importantly, to prevent secondary electrons to escape from the metallic surface.

To this end two approaches have been used: one side by covering the tip with Cathodic or Anodic Electrophoretic paint and on the other by depositing a layer of parylene. Then the main issue is to be able to obtain a tip with an apex open.

For capacitance measurements (WP4), metallic tips have been prepared by etching thin 20 µm diameter tungsten wire. Tips were then glued to the tuning fork, which in turn was fixed by magnets to the microscope head (see fig. IV.3). Gluing thin tips permit to conserve a quality factor of the tuning fork as high as 10^4.

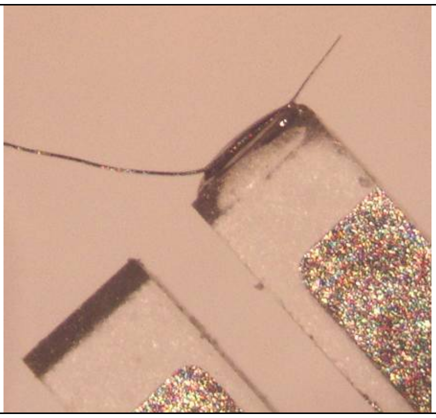
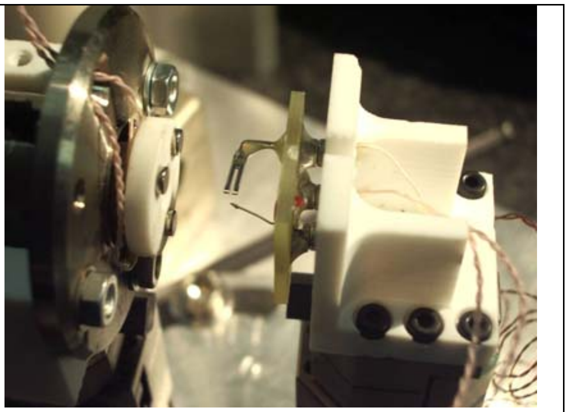
	

Figure IV.2a 20 µm diameter tungsten wire glued just after etching on the tuning fork (perpendicular geometry).	**Figure IV.2b** Tuning fork in perpendicular geometry magnetically clamped on top of *Attocube®* positioners.

IV.1.1.2 Optical fiber tips

Fiber tips are much more complicated to sharpen than metallic tips. Pulling and etching tests have been done in the Marseille and Trento laboratories; coating and characterization tests of the obtained optical fiber probes were performed at the University of Tartu and at ISSP in Riga, using a purpose-built instrumentation (see figure IV.3).

Fig. IV.3 *Evaporation chamber and coating equipment developed at the University of Tartu*

Eventually the idea to fabricate the optical fiber tips in house has been discarded, as well as the proposal to append to the X-TIP project another contractor expert in fiber production. In the last year the adopted solution was to get two kinds of commercial fibers from two commercial companies specialized in this domain and testing them in the different labs.

The first is represented by chemically-etched optical fiber tips, produced by NT-MDT. A thin aluminum coating is evaporated on the tip, whose aperture diameter is generally between 30 and 100 nm. The nominal optical efficiency goes from $3\text{-}30\times10^{-5}$ for a 100 nm aperture to $3\text{-}30\times10^{-6}$ for a 30 nm hole. The curvature radius and the cone angle are estimated in 50-100 nm and ~20º, respectively.

The second kind of SNOM probes used with the X-TIP prototype are pulled optical fiber tips produced by LovaLite. They are obtained from standard single-mode Corning SMF28e fibers. The apex curvature radius is about 50 nm and the tip is Al-coated. The transmission coefficient of these probes is estimated by the producer in the range $10^{-5}\text{-}10^{-4}$.

The optical fiber probes delivered by NT-MDT and LovaLite came just tapered and metallised. The WP2 X-TIP partners were in charge of gluing them to one prong of the quartz tuning-fork (see figure IV.4) and of connectorizing the optical fiber on the back side. These were the most delicate phases in the assembling of the tuning-fork and probe holder.

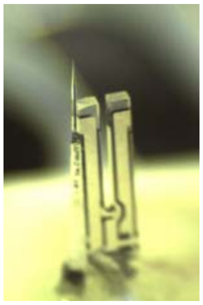


Fig. IV.4 *Zoomed view of the optical fiber probe glued on the prong arm of the quartz tuning fork*

The influence of the X-ray irradiation on the transmission of the commercial optical fibres was studied using a tungsten X-ray tube as source in Riga. The spectral measurements of luminescence from the X-ray phosphor (doped ZnS) were performed in the energy range of interest from 1.4 eV to 2.9 eV: it was found that prolonged X-ray irradiation of the fibres induced significant changes in its transparency in the red region of spectrum. Thus, the sensitivity of the optical fibres to X-rays should be considered in long time experiments, when accurate detection of luminescence intensity is required.

IV.1.2 The positioning devices: problems and perspectives

The key elements for positioning tips and samples are inertial actuators. There is a wide commercial offer, but the choice for beamline AFM is not as wide and is dictated by the following factors:

- Stiffness of the device: it should not move or slip when jerked by endstation motors
- Easiness of drive: it should be driven by the electronic that controls the entire instrument
- It should be vacuum compatible. It should have a minimum of repeatability

We tested a good number of devices and selected the ones which better fit these different needs. Nevertheless, for optimal results of commercial future units, the positionners will be custom made for a maximum of rigidity.

IV.1.3 The electron detection chain

In order to be able to detect current in the order of picoAmperes we are using a lock-in detection system. We modulate the incoming photon beam with a mechanical chopper and detect the electrons generated with the same frequency using a lock-in amplifier. All these equipments are remotely controlled during all experiments. This implied a lot of control software development.

IV.1.4 Total yield measurements

IV.1.4.1 Total Yield Simulations and experiment

During the first year two computer codes, “Penelope” and “EGSnrc”, were used to perform Monte Carlo simulations to evaluate the number of photoelectron ejected from a surface illuminated by X-rays.

Simulations have then been counterchecked using the Faraday cap geometry (Fig. IV.5), during an experiment on a Bending Magnet beamline BM05.

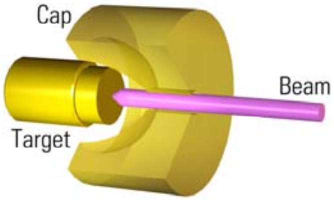


Fig. IV.5: *Faraday cap geometry.*

As shown in the figures IV.6 and IV7 the results agreed quite well. At the L_2 absorption edge of gold (13.73 keV) with an incident flux of ~10^8 phs/sec, we can clearly observe an absorption jump of about 180 fA. The Monte Carlo simulations show a jump of the same order of magnitude. The difference in the slope at the jump edge is due to the fact that Monte Carlo codes are not taking into account electrons with energies below 100 eV.

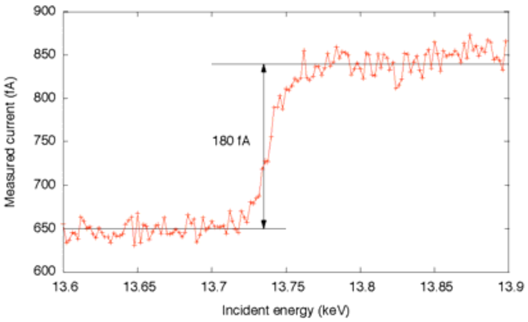


Fig. IV.6: *Measured current*

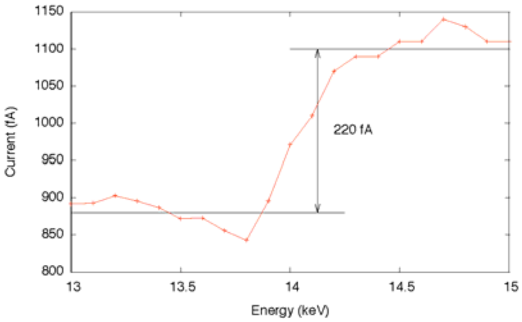


Figure IV.7: *Simulation with EGSnrc*

It should be noted though the small value of currents for 10^8 ph/sec. On the most performing beamlines the number of photons cannot be more than three-four orders of magnitude higher.

IV.1.4.2 Experimental setup

During the second year of the project, the experimental set-up shown here on fig. IV.8. was mounted and tested. The chopper is used to modulate the beam to be able to collect through the lock-in amplifier only the signal really linked with the impinging radiation. The chopper frequency is of few kHz and is far away from the natural frequency of the tuning fork at 32.750 kHz to exclude any cross-talk.

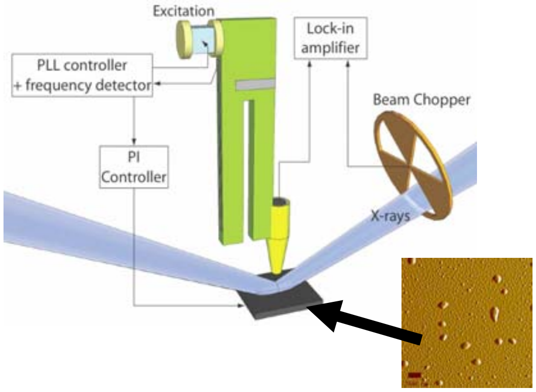


Fig. IV.8: *Experimental setup geometry.*

IV.1.4.3 Alignment procedure

Aligning focal spot (few microns), tip (even less than few micron) and sample on the same location is not easy and a procedure using both the drain currents induced by the beam and the fluorescence emitted by the tip and the sample has been defined. The picture below describes graphically the procedure.

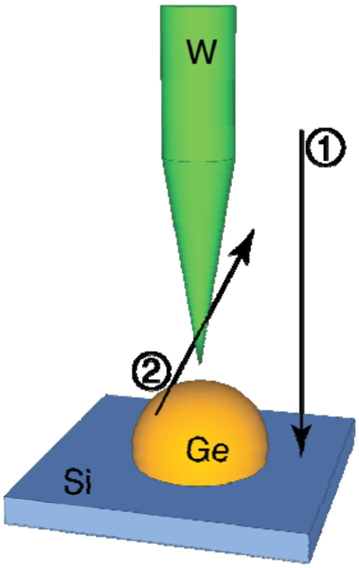


Fig. IV.9 *Arrow #1 and #2 corresponds to fig. IV.10 and IV.11 for displacements with respect to the beam.*

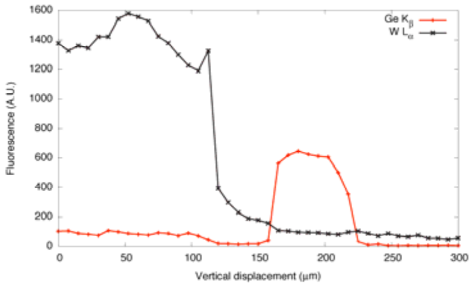


Fig. IV.10 *Fluorescence signal for a vertical displacement with respect to the beam (Arrow #1).*

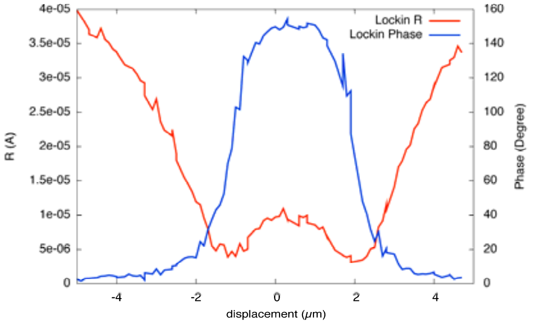
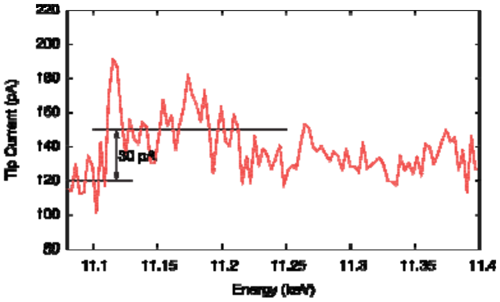


Fig. IV.11 *Current signal for a horizontal displacement with respect to the beam (Arrow #2).*

IV.1.4.4 Total Yield experiments on Nano-particle

However, on the first test on an Insertion Device beamline, ID22, we got the spectra here below (fig IV.12), extremely noisy indeed. The grazing incidence of the beam on sample, the dispersion of the Ge dots we were looking at, and the general noise at the beamline justified in part the noise, but indicated us also that a lot of work was still to be done.



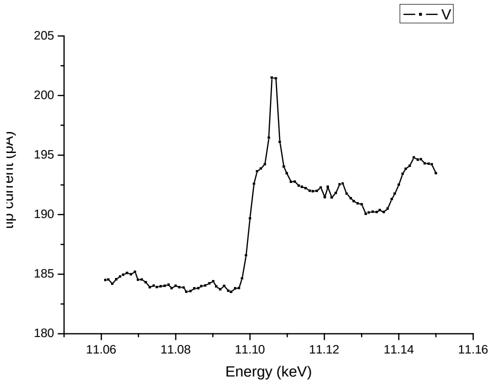


Fig. IV.12 *Result obtained during the first experiment.* **Fig. IV.13** *Result obtained during the last experiment.*

Consistent results were obtained starting from the third year, when all the details of the electronic chain were optimized.

The spectrum on Figures IV.13 indicates how the quality of the collected data improved in the last year. The spectrum is from an array of Ge nanodots and the XAS data in Total Yield indicate that the dots are strongly oxidized.

IV.1.4.5 Lateral resolution

The lateral resolution is still an open issue.

The last experiments on beamline indicate a lateral resolution of few nanometers and “smart” tips are in preparation to limit the area of collection of the tip.

The last tips are prepared by immersion of the tip in UV curing glue that leaves just the extreme end of the tip free.

IV.1.5 *Capacitance measurements (WP4)*

The goal of the WP4 is to develop SPM instrument having element-specific contrast via x-ray induced changes of capacitance, conductivity or charge on the sample surface. The schematic view of the head prototype and of the detection/analysis setup is shown in Fig. IV.14.

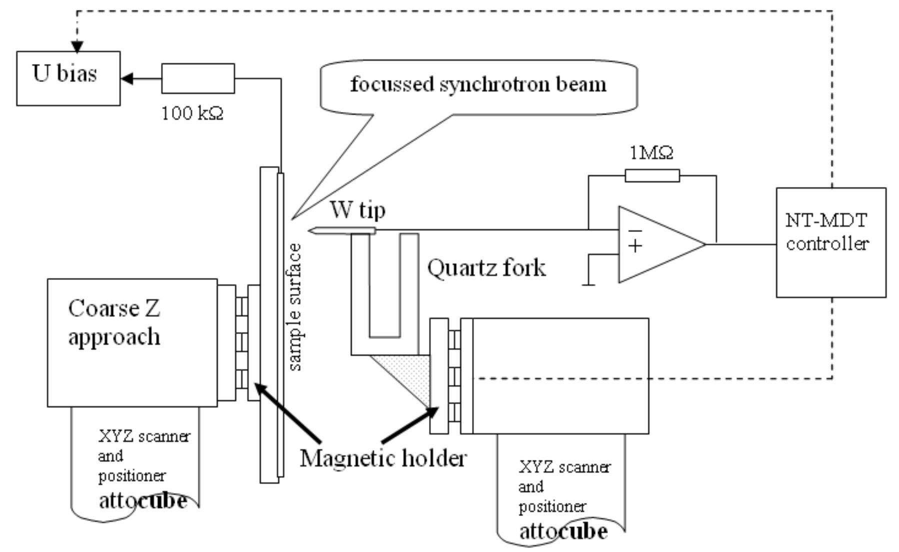


Fig. IV.14. Experiment layout for current measurement using external current-voltage preamplifier and NT-MDT controller.

Laboratory tests of the prototype were done by measuring the intermittent contact of the tip with a conductive surface (gold) at room temperature. Resolutions of surface details below 100 nm were observed (Fig. IV.15).

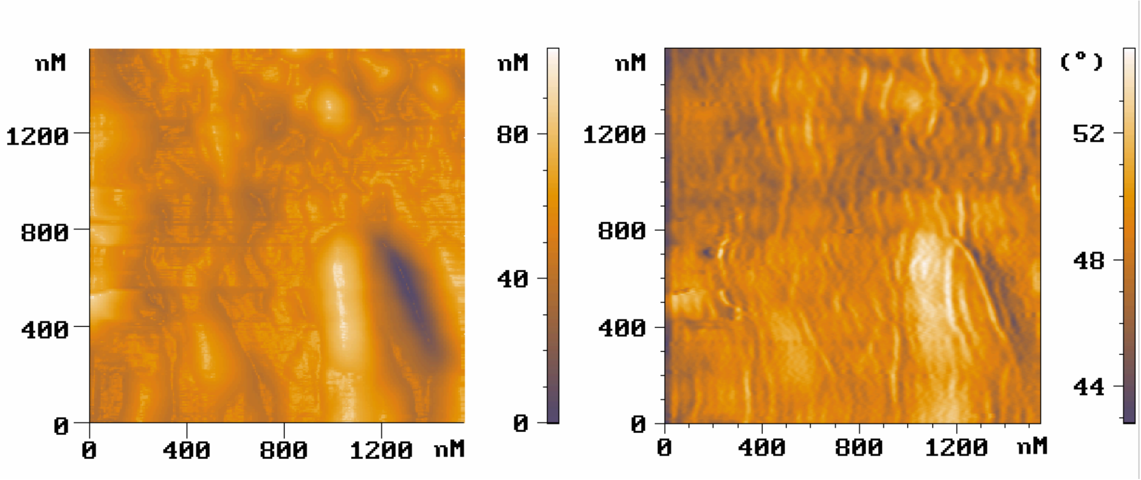


Fig. IV.15. Topographic image of a gold surface (left) and corresponding phase picture (right) scanned with a conductive tip working in oscillating mode in perpendicular geometry. Noise is due to tip-surface contact instabilities due to gluing problems.

Synchrotron radiation tests of the capacitance prototype have been performed at ESRF BM08 beamline using the tuning fork in perpendicular geometry. Unfortunately the harsh environment of the beamline in terms of vibrations and radiation showed the difficulty of the measurements. The lack of further testing beamtime has hindered any subsequent improvement of the prototype.

In view of these experimental difficulties it has been recognised within the project that force measurements are easier to carry out than capacitance measurements when synchrotron radiation is involved.

Within WP4, laboratory tests in Electromotive Force Microscopy (EFM) and Scanning Capacitance Microscopy (SCM) have been conducted in Tartu University with commercial instrumentation. Some results are reported in Fig. IV.16 below.

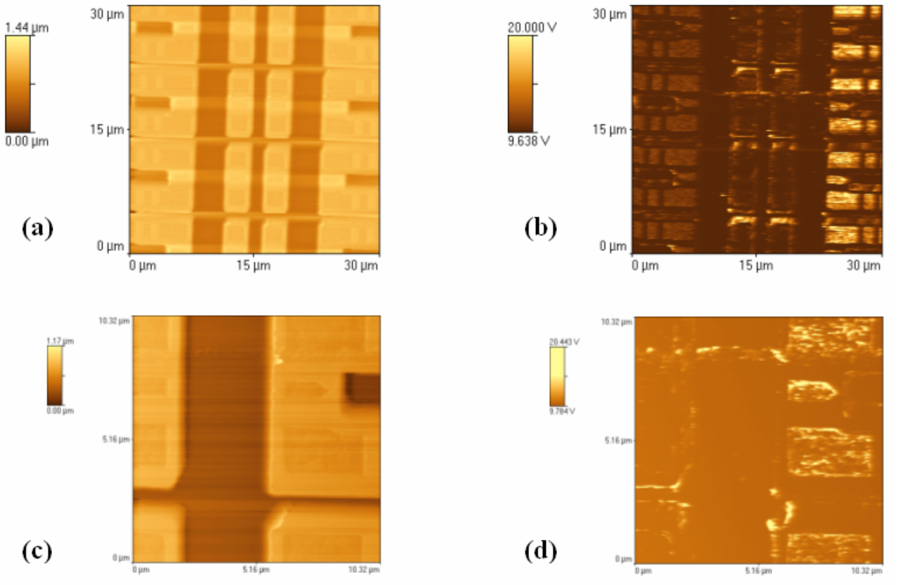


Fig. IV.16 Investigation of a SCM test sample (Veeco) in topographic (a and c) and SCM modes (b and d): lighter areas have larger capacitance and then higher doping levels. a, b 30x30 µm$^{2.}$ c, d- 10x10 µm^2

V X-ray excited optical luminescence (XEOL) measurements

The goal of the WP2 was to collect X-ray excited optical luminescence (XEOL or PLY, Photoluminescence Yield) in near field conditions by the way of a sharpened optical fibre: in such an experiment the apex of the fibre also plays the role of a topographic probe. Thus topographic mapping is simultaneously complemented by optical imaging, and chemical mapping is performed with the lateral resolution of the SNOM tip.

We present here a summary of the main experimental results of the WP2.

V.1 XAS-SNOM experimental setup

During the three years of the X-TIP project, different XAS-SNOM microscope heads were developed, characterized at ESRF and progressively improved. The instrument, as it looks in its final version, is sketched in figure V.1.

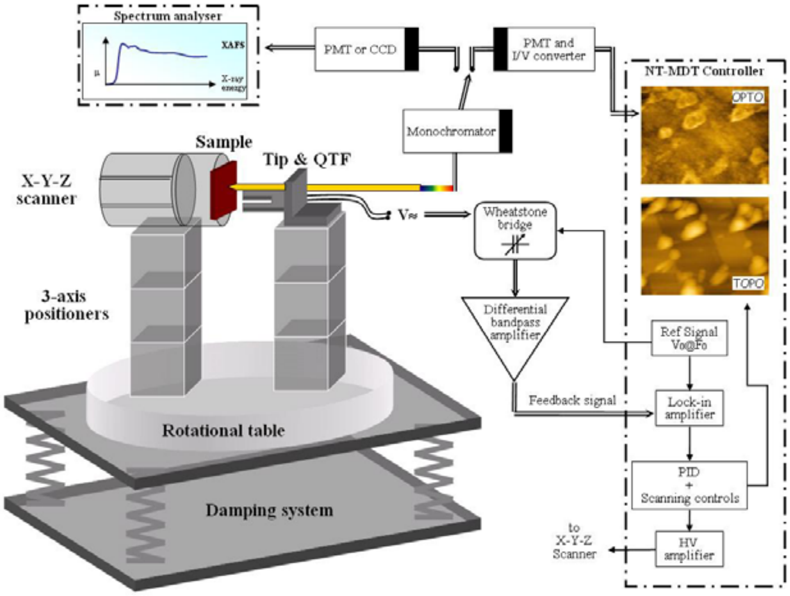


Fig. V.1 Scheme of the XAS-SNOM head prototype and XEOL detection/analysis setup as it looks in its final and improved version.

Two towers of ultra-compact piezoelectric actuators provide the microscope with a 6-independent-axis nanopositioning system that allows the absolute alignment of the sample and of the probe with respect to the synchrotron radiation beam. The Attocube tower that holds the sample is provided also with a commercial NT-MDT scanner employed for the imaging. The probe engagement on the sample surface and the probe-sample distance regulation during the imaging are controlled by means of the Z movement of the piezo-scanner. The X-TIP instrumentation is completed by a sturdy circular base that gives stability to the microscope head and allows changing the incidence angle of the beam on the sample. A damping system attenuates the mechanical vibrations, uncoupling the device from its support. An external compact box contains the electronics of the shear-force feedback system.

The voltage signal of the quartz tuning-fork is monitored by the NT-MDT controller. A PID loop acts on the probe-sample distance, recording the topographical image of the sample surface. The same NT-MDT controller accepts as input also the light signal collected by the fiber tip to register the optical image of the sample surface. On the other hand, the XEOL and XEOL-XAFS spectra are recorded and displayed by dedicated software, after undergoing a specific spectral analysis. The photon detection is carried out by means of a spectrograph/monochromator, a CCD camera (for fast spectral analysis) and two photomultiplier tubes (for optical imaging and spectroscopic applications).

Finally, the integration of the X-TIP instrumentation with the beamline software control and data acquisition system required the development of a specific protocol based on the setting and analysis of some digital lines. This allowed a simple and secure implementation of the X-TIP experiment at different beamlines of a synchrotron radiation facility.

V.2 Alignment procedure of SNOM tips on a synchrotron beamline

Compared with the case of electron measurements, photon detection needs a completely different alignment procedure of the optical fibre probe. The goal of the alignment procedure is twofold: (1) to position the apex of the tip (a few tens of nm) in correspondence of the focusing point of the X-ray beam (a few microns in size); (2) to minimize the irradiation of the fiber tip by the beam in order to reduce the contribution of the probe to the XEOL signal.

To this purpose, a laser light previously aligned with the synchrotron radiation beam served as guideline to carry out a first placement of the tip on the beam. Then a Si detector placed after the prototype measured the X-ray absorption due to the presence of the tip while it was scanned along the two transversal directions, as shown in figure V.2 The plot of the diode currrent as a function of the distance covered by the probe indicated not only the optimal position of the tip relatively to the X-ray beam but provided also a cross section profile and an indirect measure of its size.

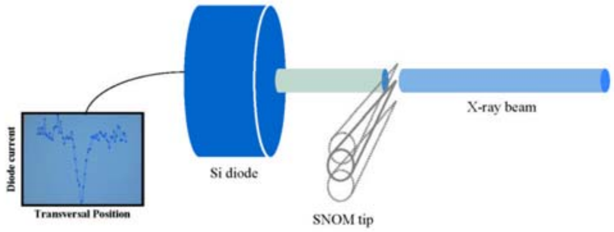


Figure V.2 Scheme of the beam-tip alignment procedure employed at ESRF.

V.3 Optical Luminescence experiments.

A number of ZnO, $ZnWO_4$ and mixed ZnO-$ZnWO_4$ samples suitable for a demonstration of XEOL-SNOM prototype operation at the synchrotron and laboratory setups were produced at the ISSP (Riga), Marseille and Trento laboratories.

Special test samples, based on $ZnWO_4$ thin film scintillator, were also developed and produced at the ISSP (Riga) by electron beam lithography using scanning electron microscope (SEM) facility. These samples can be used for testing/calibration of the SNOM microscopes under X-ray/UV excitation (near-field photoluminescence detection) or visible laser excitation (near-field Raman signal or optical reflection detection).

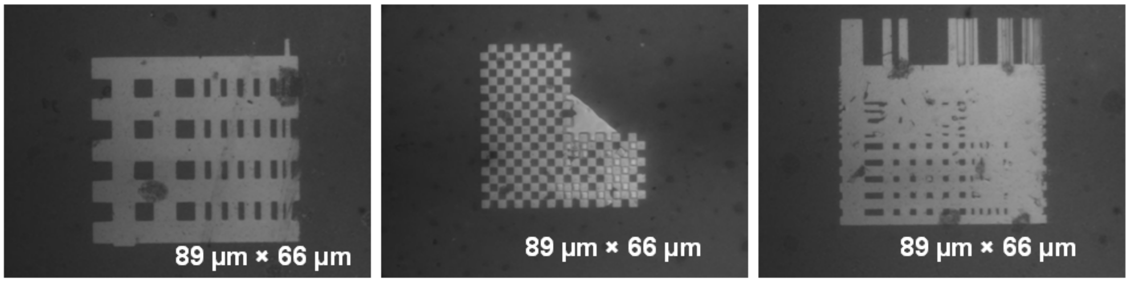


Fig. V.3 *Multipurpose test samples of patterned luminescent thin films for scanning near-field optical microscopy produced by electron beam lithography at ISSP (Riga). Images sizes: 89 µm × 66 µm.*

Two different kinds of experiments were accessible: element-specific profilometry and local XEOL spectroscopy.

V.3.1 Element-specific profilometry

The XAS-SNOM prototype has been used to carry out experiments of element-specific profilometry, consisting in a conventional scanning microscopy technique enriched by sensitivity to chemical elements distribution. This is achieved by tuning the X-ray energy below and above the absorption edge of a specific element and by detecting the X-ray excited optical luminescence in near-field conditions while scanning the sample surface with the probe. The optical contrast, obtained subtracting the images above and below the absorption edge, provides the chemical map of the selected atomic species on the sample surface, with the spatial resolution offered by the tip. In addition, a thorough comparison of the optical contrasts relative to different chemical elements provides the distribution of the various luminescence phases present in the sample. As an example, in figure V.4 we report the images (18×18 μm) obtained for a mixed $ZnWO_4$/ZnO thin film deposited by dc magnetron sputtering on a Si substrate.

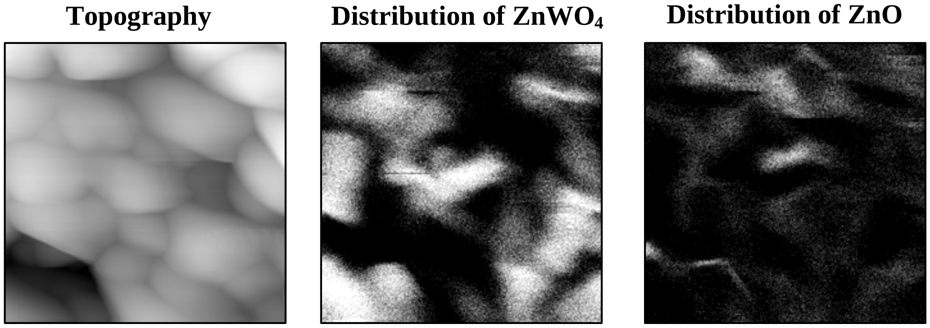

Topography **Distribution of $ZnWO_4$** **Distribution of ZnO**

Fig. V.4 *Topographic image (left) and distribution of the luminescent phases (center and right) for a mixed $ZnWO_4$/ZnO thin film. All images (18×18 μm) refer to same region of the sample.*

The topography (left) reproduces the micro grains sputtered on the surface. The other images (center and right) derive from the analysis of the XEOL optical contrasts at the Zn K- and W L_3-edge. They give information on the distribution of the $ZnWO_4$ and ZnO chemical compounds on the surface, with the nanometric precision provided by the employment of the fiber tip as detector of the optical signal. Since the XAS-SNOM microscope performs simultaneously the optical and topographic imaging, all images in figure V.4 refer to same region of the sample, thus allowing a comparative study of morphology and optical properties of the sample.

V.3.2 Local XEOL spectroscopy

Local X-ray absorption measurements in near-field XEOL detection mode were also performed at ESRF by means of the XAS-SNOM prototype. The optical fibre tip was placed in a point of interest of the sample surface and kept in near-field condition while the X-ray energy was tuned across the absorption edge of a selected chemical element. The XANES spectrum was obtained by monitoring the XEOL intensity at a fixed wavelength as a function of the X-ray energy.

Figure V.5 shows the spectra at the Zn *K*- and W L_3-edge obtained for the $ZnWO_4/ZnO$ nanostructured thin film presented above. To our knowledge, this is the first time that near-field XANES-XEOL spectra are recorded by means of a custom-tailored SNOM microscope integrated on a synchrotron radiation facility. Black and red lines refer to spectra acquired at different points of the sample surface. The differences exhibited by these spectra (in particular at the Zn *K*-edge) indicate the potentiality of this technique for studying the local environment of a chemical element and the related optical properties of the sample with the spatial resolution of the optical fiber probe. This represents a novel and promising application of conventional X-ray absorption spectroscopy technique in XEOL detection mode.

The reproducibility of all acquired spectra has been checked out, obtaining positive and promising results in terms of system and X-ray beam stability. A much higher signal-to-noise ratio has been observed when a more intense synchrotron radiation beam has been used, namely passing from an exciting source of 10^{13} ph/s·mm^2 (ESRF-BM05) to one of about 10^{15} ph/s·mm^2 (ESRF-ID03). As a direct consequence of the XEOL signal enhancement, the XANES-XEOL spectra exhibit more defined and better resolved modulations of the absorption coefficient.

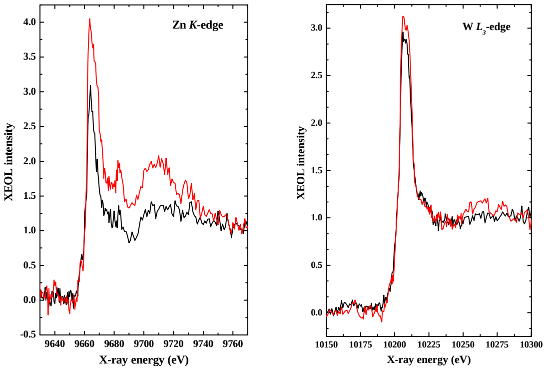


Fig. V.5. *Local XANES-XEOL spectra at the Zn K and W* L_3*-edge of a* $ZnWO_4/ZnO$ *nanostructured thin film. Black and red lines refer to spectra acquired at two different points of the sample surface. All spectra have been normalized at the edge-jump.*

V.3.3 Spatial resolution

In a conventional laboratory environment, the microscope prototype exhibits extremely good imaging capabilities. Figure V.6 shows the simultaneous topographic and optical images of stoichiometric ZnO nanoparticles dispersed on a silica grating. In both cases, a lateral resolution of about 100-200 nm is commonly achieved with this setup while in the vertical direction the resolution is limited by the noise of the piezo-scanner (2-3 nm).

The same spatial resolution has been achieved also at ESRF with the employment of a custom-tailored damping stage, specifically developed to attenuate the mechanical vibrations typical of the harsh synchrotron radiation environment.

Despite, the desired lateral resolution of 50 nm has not yet been achieved, the results obtained so far are promising in terms of system stability and optical fiber probe potentialities.

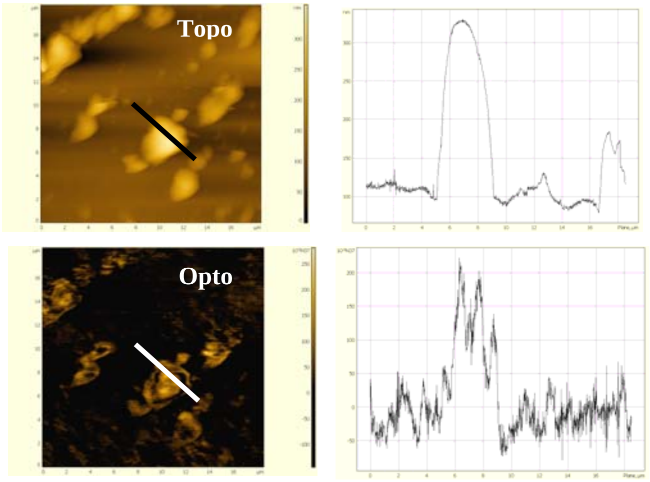


Fig. V.6 *Couple of topographic-optical images (18×18 µm) and arbitrary section profiles for stoichiometric ZnO particles randomly dispersed on a silica grating. A CdTe laser has been used as exciting source.*

VI Scientific and instrumental impact and outcome of WP1, WP3 and WP5

This chapter gives an overview of the achievements of the combined WP1, WP3 and WP5 packages with the idea of presenting coherent panoply of the possibilities opened by X-Tip. Therefore the chapter will focus less on the technical details or on the difficulties encountered and the way to contour them that could be found in the activity reports.

Put together, the three work packages were intended to define, manufacture and assess an instrument sensed to serve the following objectives:

1. Image at the nanoscale both the sample and the X-ray beam in order to bring the latter to impinge where the tip is.
2. Use the tip as a detector whose lateral resolution is defined by the tip size and not by the beam focal spot.
3. Induce with the tip local changes in the sample and monitor the results in real time by X-ray diffraction or scattering
4. Enter in the domain of force control for manipulating object at nanoscale

The first picture of this chapter illustrates how the **first** objective has been reached:

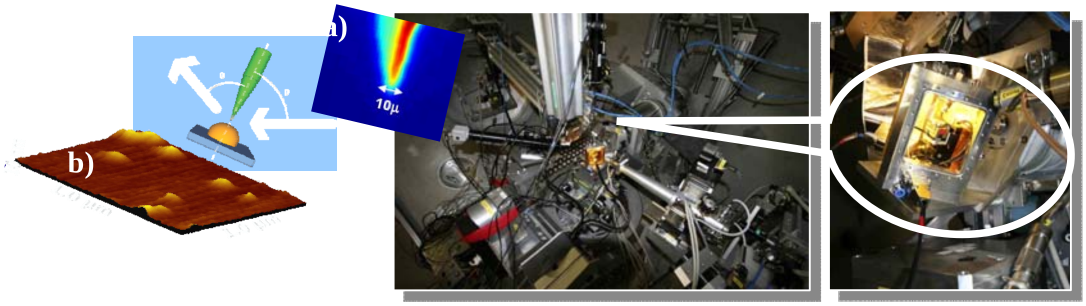


Fig VI.1 *On the left the basic set-up of a Beamline AFM: the tip can either be scanned through the X-ray beam cross-section producing the beam image shown in a), or the sample can be rastered below the tip to produce the surface topography in b). These two steps are essential to align the desired nano-feature under the beam and the tip. The right panels of the picture show the BL_AFM mounted on the diffractometer of a beamline.*

The BL-AFM is then a fundamental instrument for the study of nano-objects under X-rays that would not be visible with other tools other than expensive and bulky SEMs.

Its limited size and flexibility permits its installation in virtually any beamline with limited changes to its architecture.

The **second** objective was more ambitious because of noise problems. Nevertheless the problems have been solved during the third year. The contributions to the spectrum reported in the chapter Total Yield measurements/Experiments have been estimated to come from an area of about 10 micron. Further reduction in lateral resolution (and increased noise) will be obtained with insulated and recoated tips presently under preparation.

But with the experience we learnt that much higher signals and better accuracy could be obtained if diffraction and tip detection were used in a way that well different from the "canonical" one. If one has a distribution of diffracting nano-object in the near field the bunch of diffracted beams will have the same distribution of the nano-objects projected against the propagation plane of the diffracting beams. In the far field the beam would merge together because of the divergence of the beam, and even with a 2D detector with infinite resolution it

would not be possible to isolate the contribution of a single nano-object.
A very tiny tip, instead, can act as a detector in the near field with a resolution defined by its size. Experiments have been conducted on a distribution of Ge dots on Si and as the picture below indicates, the diffracted beam shows a granularity very similar to the one of the sample as seen by the same BL-AFM.

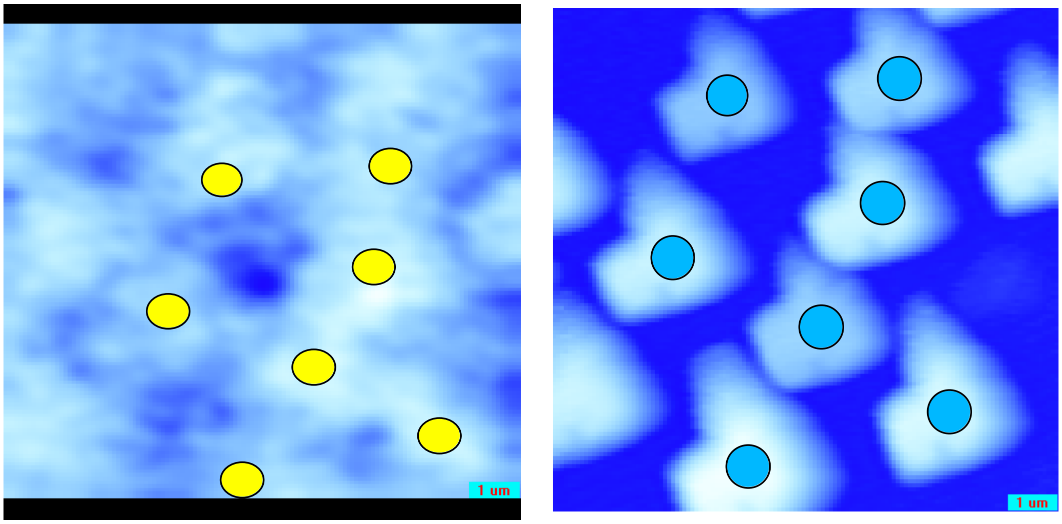


Fig. VI.2 *on the left: diffraction image from a distribution of dots as seen in Diffraction Near Field by a BL-AFM tip. On the right, dots distribution as seen by the same BL-AFM in topographic mode.*

The third objective aimed at interacting with the sample in order to induce local deformations following them in real time via X-ray scattering. An example of the application is presented in figure VI.3.
In the picture, one island from an array of many is aligned to the X-ray beam thanks to the BL-AFM. In the reciprocal space around a substrate Bragg reflection the contribution from that specific island is monitored. The tip is then used to remove the island and the change on the diffraction pattern recorded in real time.

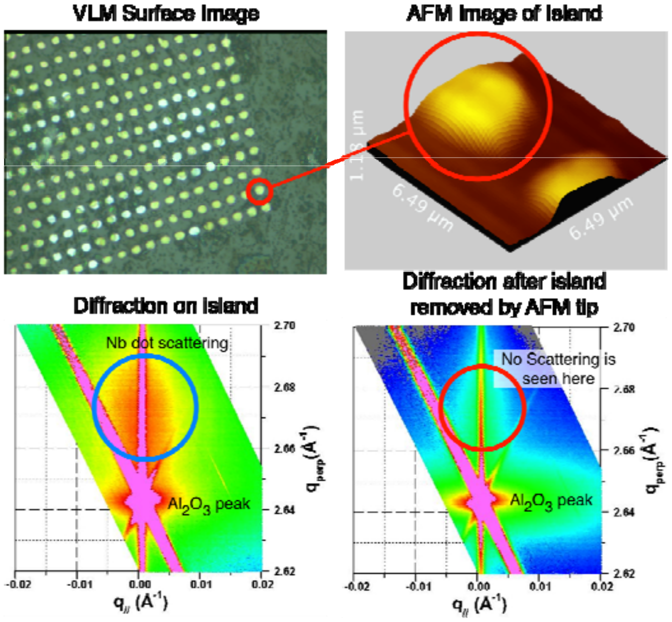
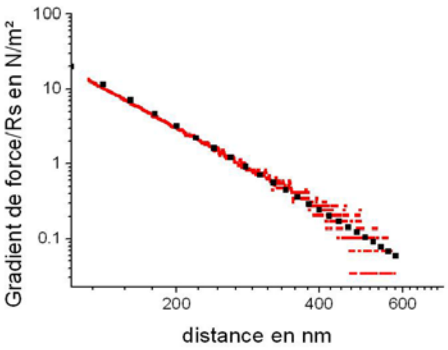


Fig. **VI.3**: surface manipulation and induced deformation

All the objectives 1, 2 and 3 were reached with a single instrument, the basic BL-AFM.
Other two microscopes were built often recycling components of previous tests.
These two extra microscopes are intended to explore and exploit the force field between objects at nanometric scale for furthering the experience gained in the X-Tip project.

The second prototype, here on the side, is a UHV vacuum AFM that can measure forces between tip and surface by detecting the deflection of an AFM cantilever through a fiber optic based Fabry Perot cavity accommodated on the back on its back face. It gives the possibility to do true AFM measurements (contact and non contact AFM) in an X-ray beamline with the possibility of measuring the associated force field. The measurable forces range from nanonewton down to femtonewton with a limit classically determined by thermal vibrations.
In future Synchrotron Radiation experiments the holding and handling of nanosized objects is very important, since the X-ray charges the particles that tend to run away. Full control of the forces exerted to hold them is then necessary. The second prototype has been used then to study these forces in details. As an example of the reached performance in this critical area, we have made a quantitative measurement of the Casimir force from 50 nm up to 500nm in the sphere plane geometry. Such measurements with an error bar around 5% in AFM dynamic mode are presently at the state of the art.



These developments represented a key step in the combination of force measurements with nanopositioning to enter the characterization of Micro and NanoMechanical Systems. In this field, the use of X-ray absorption and/or X-ray diffraction to probe MEMS or NEMS properties is just at the beginning.

To push our instrumental capability in associating force detection and X-ray to the limits, we observed the mechanical interaction between X-rays and a tiny germanium block glued to the extremity of an AFM cantilever provided with a Fabry-Perot interferometer read-out on its back. The experimental arrangement is shown on figure VI5. The blue vertical blade is the cantilever (350x35x5 micron), the Ge block is represented in red, the X-ray beam in blue and the Fabry-Perot optical fiber in grey with an orange core.

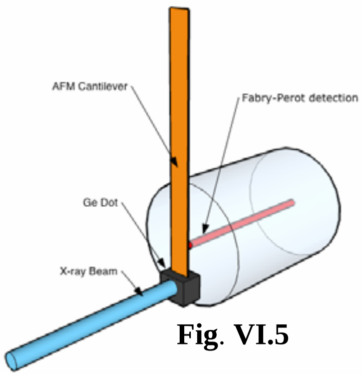


Fig. VI.5

The X-ray beam is chopped at the natural frequency of the cantilever-Ge system (2-3 kHz following the type of cantilever) and the Fabry-Perot output is measured via a lock-in amplifier.

The aim of the experiment is to couple the microcantilever to the X-ray beam through a well identified electronic transition: the germanium K-edge threshold.

The energy of the inpinging beam is then swept through the 1s absoption edge at 11 100 eV while the amplitude of the cantilever oscillation is recorder by the interpherometer.

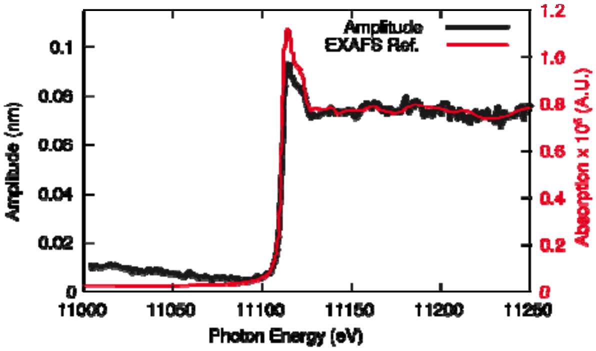


Fig. VI.6

As shown in the figure VI.6 above, the oscillation amplitude well reproduces the EXAFS features. The error bar is of 5 picometers over a “mechanical edge jump” of about 200 picometer.

In this first experiment the excitation is due to mechano-elastic coupling to the X-ray beam.

VII Scientific and instrumental impact and outcome of WP2

Here we give a short overview of the main achievements of the WP2 package, on the basis of results obtained at the synchrotron beamlines of ESRF.

The main scientific objective of WP2 was to demonstrate the possibility to detect in the near field the light emitted under X-ray excitation at synchrotron radiation facilities.

This has been fully achieved by using the XAS-SNOM microscope head in two different kinds of experiments:

a. At first, by scanning the sample under the tip, SNOM and topographic images were collected at the same time. The possibility to tune the X-ray beam at different excitation energies (covering for example Zn and W edges for mixed $ZnO/ZnWO_4$ films) and to select a wavelength of the photoluminescence, allowed to collect different SNOM images (imaging mode);
b. Then X-ray absorption spectra (XAS) were measured by scanning the energy of the X-ray beam and collecting the luminescence in near-field configuration in a given place of the sample (spectroscopy mode).

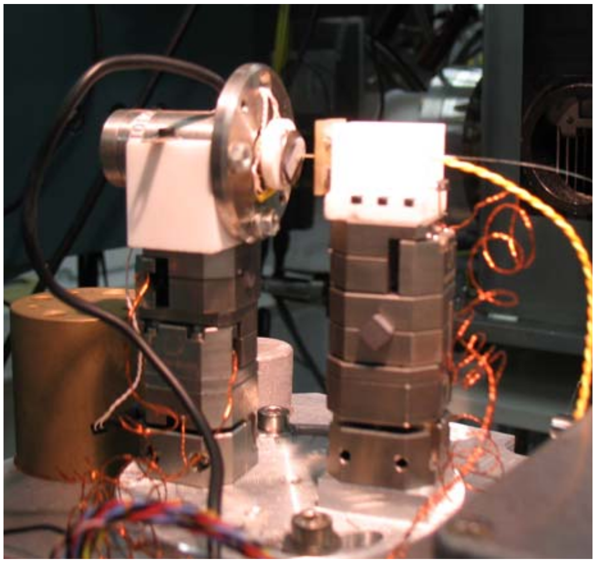


Fig. VII.1 *Third XAS-SNOM prototype developed by the WP2 team in Marseille.*

The dedicated SNOM microscope head is ready to be used in different beamlines and experimental vacuum chambers. It is mounted on a rotating table to roughly change the relative orientation of sample surface in respect to the X-ray beam; it allows a fully independent alignment of the tip (in respect with the X-ray beam) and of the sample (under the tip), with a user-friendly software interface. The reproducibility, stability and lateral resolution of the instrument have been tested with success: the main limitations originate from the mechanical vibrations of the experimental tables inside the hutches of ESRF.

Great experience has been gained on the general problem of tip degradation during the measurements, in particular under X-ray irradiation. For the success of the more interesting experiments (in particular for XAS measurements), the very high incoming photon flux available at ID03 was necessary. However, the luminescence of the tip itself under very intense X-ray beam imposes a finite limit to the sensitivity of the SNOM imaging.

In summary, when the intensity and spectral properties of the photoluminescence is dependent on the absorbing atoms (and, better, on their local environment), it is possible with the XAS-SNOM head to align under the X-ray beam a particular region or nanostructure present on the sample and to detect in near field the XEOL signal. Since this signal is dependent on the X-ray energy and on the local structure around the emitting centres, we have thus many possibilities to reconstruct an image of the sample: by topography, by comparing optical images obtained with different X-ray excitation, by comparing optical images obtained with an appropriate wavelength selection of the photoluminescence.

For example, in mixed ZnO/ZnWO4 films, by comparing different optical images, we were able to obtain maps of Zn and W distribution and, more appealing, further maps of ZnO and $ZnWO_4$ distribution. The intrinsic resolution of these maps is determined by the near-field characteristics of the tip.

A second important point is the possibility to obtain high quality XANES spectra using synchrotron radiation as exciting source by collecting the XEOL intensity in the near field. This allows the study of the local atomic structure and electron density of states of the absorbing atoms present near the optical emission centres. Note that this kind of experiments is strongly sample dependent because the XEOL process (and its dependence on X-ray energy) is quite complex and difficult to be controlled in advance. For instance, when investigating dispersed or isolated nanostructures more difficulties arise, mainly related to the very weak XEOL intensity. The success of further studies to gain deeper insight into this field is conditional on the availability of beamtime long enough to carry out experiments using an intense, focussed X-ray synchrotron radiation beam. Time-resolved XEOL detection may also be explored in the future.

VIII Dissemination and outlook

The X-Tip project has provided the necessary support and freedom to develop an idea that for long time stayed underdeveloped: the association of *in situ* real-time Scanning Probe Instrumentation with X-ray Spectroscopies and Scattering techniques.

The project went even further, showing the path to get a hold into manipulation and handling of nanosamples with controlled forces.

The first part of the project, association of SPMs and X-rays, has gained its notoriety among scientists at the ESRF and other facilities for the simplicity in installation, easiness of operation and flexibility.

At the ESRF four BL-AFM units are being developed and installed on beamlines through the creation of a commercial company charged of developing BL-AFMs and developing the concept of cold damped AFM that has been patented in the frame of the X-Tip project and that will be essential in the manipulation of nano-objects.

The spin off company, Small Infinity, has been already assessed by the regional authorities and awarded a number of grants for innovation.

The detection of optical photon has shown all its potentialities in giving the necessary contrast. The SNOM-XEOL apparatus that has been developed can already be installed in existing beamlines. In the last months the market of sharpened fiberoptics tip has shown new activity, and high quality tapered fibers will be soon on the market, making the retrofitting of the BL AFM with fiber easier.

The future developments that will stem out from X-Tip will have two distinct characters: one characterized by highly sophisticated application in molecular sensing and handling under SR beams, and the other addressing laboratory applications for nano-materials.

VIII.1 Outlook in SR

Figures VIII.1 below are taken from the “Purple Book”, a recent issued thick publication that envisages the scientific developments of the ESRF for the next 10 years. The pictures indicate the critical ingredients that underpin the scientific and technological advancement of synchrotron radiation research. The left panel summarizes the level of integration necessary among different instrumentation. Here positioning, manipulation and feedback are, with optics and detector, the main ingredients of the entire game, where stability and reliability play the main role.

The right panel sketches the multimodal approach to sample analysis where many other techniques should integrate the X-ray in the characterization of materials. Again, among them, AFMs, application of strain and morphology analysis occupy a central role.

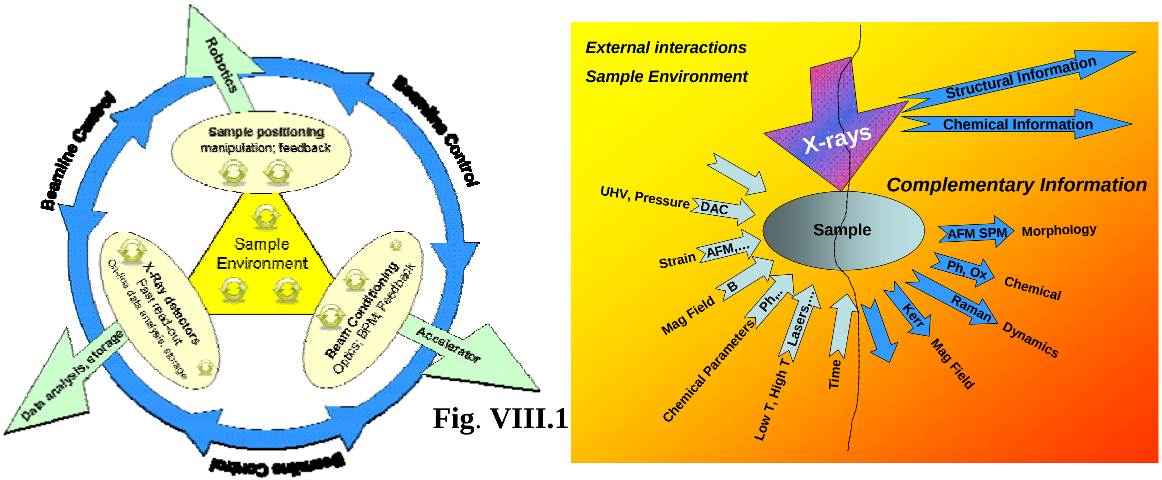


Fig. VIII.1

The work carried out with X-Tip addresses exactly these problems: the BL-AFM responds to the needs of navigating the surface and applying local stresses and the cold damping mode opens the way to overcome thermal excitations in sensing tiny forces.
Nevertheless the manipulation of nanoparticules is still an open issue. The studies of NEMS and MEMS done in the frame of X-Tip are just the beginning of the path.
Again from the Purple Book an idea that matured within the X-Tip effort: a NEMS structure that can navigate the surface of the nano-object and on the basis of tribological and morphological information permits the reconstruction of a virtual reality where the “explorer” can intervene through haptic control of a set of nano-tweezers.

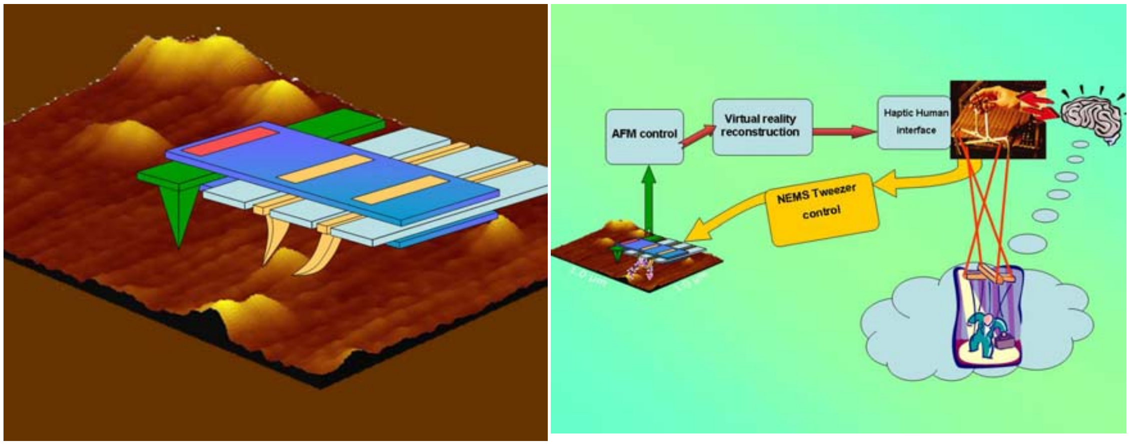


Fig. VIII.2. The figure represents the concept of a nano-gripper and its functional scheme: the tip of an AFM (in green) explores the sample surface in terms of morphology and rheological characteristics. Through a reconstructed virtual reality interface the user can haptically interact with the nano-objects on the surface.

We are not there yet. The ideal model of nanogripper shown on the left here below is for the moment at its first prototype as shown on the right.

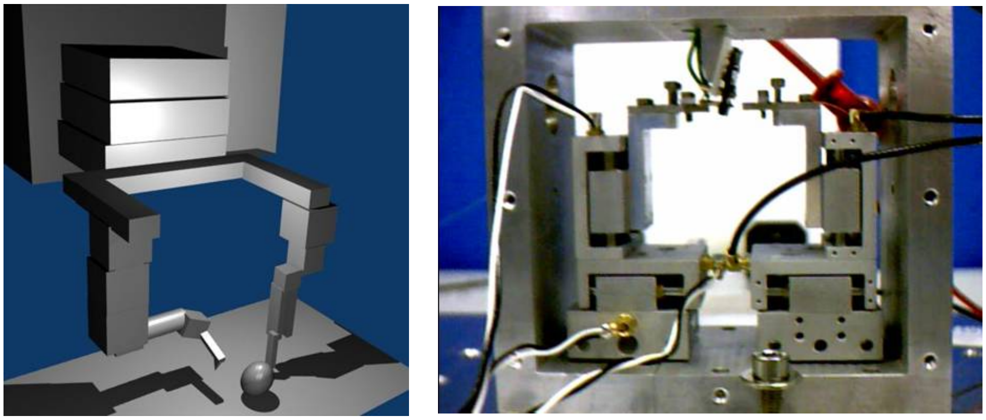


Fig. VIII.3

The prototype is now used to probe dynamical properties of MEMS and NEMS on the basis of optical detection and actuation on daily basis.

VIII.2 Outlook in the laboratory

The X-Tip was also expected to check the possible use of Tip based technologies in laboratory based X-ray instrumentation.

We strongly believe that the technology developed can well be applied to laboratory X-ray generators.

In morphology mode the BL-AFM can be easily adapted to be a more generic X-ray AFM by developing custom made miniaturized inertial components.

More complicated is the issue of detection. The Total Yield detection is possible but not routinely applicable because of the low signals. Total yield emission is essentially isotropic and the number of electrons collected from the tip is then limited.

Given the directive character of diffraction phenomena, the detection of *diffracted* beams from arrays of nano-objects does not suffer from the low signal problem since the order of magnitude of the intensity of the diffracted beams is of the same order of magnitude of the intensity arriving on the crystalline dots. Local detection of these beams with a tip is probably going to raise much interest if some resources are put in its development. This would give the unique opportunity of studying diffraction from individual nano-objects with ordinary laboratory X-ray sources.

A further consideration may be expressed on the possible application of XEOL-SNOM imaging with conventional X-ray sources. The recent development of focussing techniques, especially with capillary optics, opens new perspectives in this field.

This could be an attractive industrial development of X-Tip. The availability on the same experimental chamber of both X-ray and laser focussed sources will allow performing different micro/nano-scale characterizations: standard AFM topographic maps may be coupled with SNOM or X-ray fluorescence imaging at fixed X-ray energy. The partners of WP2 are currently trying to define a new programme based on the possibility to develop an AFM head where a glass capillary is used as a topographic probe and as micro source/detector for X-rays.

VIII.3 New application in the Infrared

The X-Tip developments have been applied to sharpen the lateral resolution there where the diffraction limit forbids any good result. This is the situation in the Infrared, where wavelengths even longer than the optical ones makes impossible to focus the radiation on spots smaller than the tens of micron. As in the optical regime, SNOM techniques have been used to overcome these limits.

At the ESRF the technology developed within the X-Tip project has been used to launch a project in partnership with the group LETI of CEA and financed by that group, the ESRF and the Region Rhone-Alpes for developing an IR-SNOM instrument on the Infrared beamline branch of ID21 at the ESRF. To give more test opportunities to the instrument outside the beamtime allocated on the IR beamline, the instrument will be mounted on an OPA laser operating in the near Infrared. This will give the possibility of tuning up the instrument before the tests on the IR SR beamline.

IX Publishable results

1) As a result of the X-Tip project, a Beamline Atomic Force Microscope (BL AFM) is manufactured and commercialized by a Spin-off company named "Small Infinity", hosted in this first phase at the ESRF.

Functionalities of the BL AFM instrument:

- Rugged construction to be installed in X-ray end stations for characterization of nanosamples in the direct and reciprocal spaces. Can work in any position and during scans of the diffractometer on which is usually installed.
- Navigation over the surface of the sample for morphological and softness characterization. Reconstruction of sample morphology.
- Use of the microscope tip as Beam Position Monitors (BPMs) at the sample position for identifying the position of the X-ray beam and centering it on the desired sample feature.
- Interaction of the tip with the sample for nano-indentation and morphological modification.

The instrument is an industrial product: three prototypes have been built, one unit has been delivered and three others are in construction.
No equivalent instrument is present on the market at the moment: this is the only *instrument that can be used to look for the X-ray beam and pin it on a specific nanostructure!*

2) As a side result of the X-Tip project a "Cold Damped Atomic Force Microscope" (CD AFM) has been patented and will be available from the "Small Infinity" spin-off from late 2008 (Owners of the patent n 06/04674 "Cooling Mode AFM": ESRF, CNRS, UJF, INPG, Grenoble):

Functionalities

- Cold Damping Feedback Systems that enhance the sensitivity of AFMs to pico-forces and pico-displacements.
- AFM particularly adapted to work in liquids and on soft materials implementing a virtual non-contact tapping mode.

A prototype of the instrument has been built to verify the functionalities. The manufacturing of a demonstrator instrument is due for the first semester 2008.
This instrument is not restricted to joint use with X-ray and will have an important impact in all type of fundamental and applied research on liquids and soft condensed nanostructures.
It will offer sensitivity 100 times higher than the present generation of instrumentation.
Capital investment for marketing and distribution will be sought from mid 2008.

For further information please contact michal.hrouzek@esrf.fr

3) The third result is the development of a SNOM for XAS detection in X-Ray environments.

Functionalities

- Rugged construction for X-ray environments.
- 100-200 nm lateral resolution and about 3 nm vertical resolution.
- Possibility of element specific XAS profilometry via near field optical detection with tapered optical fibers.
- XEOL-XAS spectra obtained collecting the optical signal in near field conditions allows studying the local atomic structure and electron density of states only of those absorbing atoms that are near the optical emission centers in the small region probed by the tip. The SNOM prototype is ready to be used at the ESRF and further industrialized.

X PhD work, publications and participation to conferences

Education and Thesis work:

Silvia Larcheri defended her Ph.D. dissertation *“Joint use of X-ray synchrotron radiation microbeams and tip assisted photon detection for nano-scale XAFS spectroscopy and chemically sensitive surface mapping”* in Trento on February 28, 2007. Grant X-Tip.

Guillaume Jourdan defended his Ph.D. dissertation *“Vers un microscope de force de Casimir : mesure quantitative de forces faibles et nanopositionnement absolu”* in Grenoble on Novembre 29, 2007. Grant Univesité Joseph Fourier.

Mario Rodrigues is working on the last year of his Ph.D.: *“Nanoscale Chemical Mapping and Surface Structural Modification by joined use of X-ray microbeams and Tip assisted Detection.”* Grant University of Lisboa.

Paper Published on International Journals with Review Panel:

X-ray studies on optical and structural properties of ZnO nanostructured thin films
S. Larcheri, C. Armellini, F. Rocca, A. Kuzmin, R. Kalendarev, G. Dalba, R. Graziola, J. Purans, D. Pailharey, F. Jandard
Superlattices and Microstructures 39 (2006) 267–274

Abstract

X-ray absorption near-edge fine structure (XANES) studies have been carried out on nanostructured ZnO thin films prepared by atmospheric pressure chemical vapour deposition (APCVD). Films have been characterized by X-ray diffraction (XRD) and optical luminescence spectroscopy exciting with laser light (PL) or X-ray (XEOL). According to XRD measurements, all the APCVD samples reveal a highly (002) oriented crystalline structure. The samples have different thickness (less than 1 μm) and show significant shifts of the PL and XEOL bands in the visible region. Zn K-edge XANES spectra were recorded using synchrotron radiation at BM08 of ESRF (France), by detecting photoluminescence yield (PLY) and X-ray fluorescence yield (FLY). The differences between the PLY- and FLY-XANES confirm the possibility of studying the local environment in the luminescence centres and to correlate the structural and optical properties of ZnO nanostructured samples.

X-ray Exited Optical Luminescence Detection by Scanning Near-field Optical Microscope: a new tool for nanoscience. S. Larcheri, F. Rocca, F. Jandard, D. Pailharey, R. Graziola,A. Kuzmin and J. Purans*;* Rev. Sci. Instrum. 79, 013702 (2008)

Abstract

Investigations of complex nanostructured materials used in modern technologies require special experimental techniques able to provide information on the structure and electronic properties of materials with a spatial resolution down to the nanometer scale. We tried to address these needs through the combination of X-ray absorption spectroscopy (XAS) using synchrotron radiation micro beams with scanning near-field optical microscopy (SNOM) detection of the X-ray excited optical luminescence (XEOL) signal. This new instrumentation offers the possibility to carry out a selective structural analysis of the sample surface with the sub wavelength spatial resolution determined by

the SNOM probe aperture. In addition, the apex of the optical fiber plays the role of a topographic probe, and chemical and topographic mappings can be simultaneously recorded. Our working XAS-SNOM prototype is based on a quartz tuning-fork head mounted on a high stability nano-positioning system; a coated optical fiber tip, operating as a probe in shear-force mode; a detection system coupled with the microscope head control system; a dedicated software/hardware set-up for synchronization of the XEOL signal detection with the synchrotron beamline acquisition system. We illustrate the possibility to obtain an element-specific contrast and to perform nano-XAS experiments by detecting the Zn K and W L3 absorption edges in luminescent ZnO and mixed ZnWO4-ZnO nanostructured thin films.

Nano-scale X-ray absorption spectroscopy using XEOL-SNOM detection mode. D.Pailharey, Y.Mathey, F.Jandard, S.Larcheri, F.Rocca, A.Kuzmin, R.Kalendarev, J.Purans, G.Dalba, R.Graziola, O.Dhez. Journal of Physics: Conference Series **93** (2007) 012038

Abstract

In this report, we will present the state of the art and first results obtained with the prototype system at the synchrotron beamline ID03 at ESRF, which illustrate the possibility to obtain an element-specific contrast and to perform nano-XAS experiments by detecting the Zn K and W L3 absorption edges in mixed zinc oxide-zinc tungstate thin films.

Zn K-edge XANES in nanocrystalline ZnO.
A. Kuzmin, S. Larcheri and F. Rocca. Journal of Physics: Conference Series **93** (2007) 012045 doi:10.1088/1742-6596/93/1/012045

Abstract

Zn K-edge XANES in ZnO has been calculated within the full-multiple-scattering (FMS) and finite difference method (FDM) formalism using the ab initio FDMNES code. The influence of non-muffin-tin potential, bulk defects, surface termination and polarization effects on XANES has been analysed. The obtained theoretical results are compared with available experimental data for polycrystalline and nanocrystalline zinc oxide systems.

A new tool for nano-scale X-ray absorption spectroscopy and element-specific SNOM microscopy. S. Larcheri, F. Rocca, D. Pailharey, F. Jandard, R. Graziola, G. Dalba, A. Kuzmin, R. Kalendarev and J. Purans. Micron, to be published (2008).

Abstract

Investigations of complex nanostructured materials used in modern technologies require special experimental techniques able to provide information on the structure and electronic properties of materials with a spatial resolution down to the nanometer scale. We tried to address these needs through the combination of X-ray absorption spectroscopy (XAS) using synchrotron radiation micro beams with scanning near-field optical microscopy (SNOM) detection of the X-ray excited optical luminescence (XEOL) signal. The first results obtained with the prototype instrumentation installed at the European Synchrotron Radiation Facility (Grenoble, France) are presented. They illustrate the possibility to detect an element-specific contrast and to perform nanoscale XAS experiments at the Zn K and W L3 absorption edges in pure ZnO and mixed ZnWO4/ZnO thin films.

X-Tip: a New Tool for Nanoscience or How to Combine X-ray Spectroscopies to Local Probe Analysis, O. Dhez, M. Rodrigues, F. Comin, R. Felici & J. Chevrier, Proceeding of the 9th SRI Conference AIP 879, (2007) 1391-1394.

Charging dynamics and strong localization of a two-dimensional electron cloud; R Dianoux, H J H Smilde, F Marchi, N Buffet, P Mur, F Comin[1] and J Chevrier:
Nanotechnology **18** 325403 (2007).

Quantitative, non contact dynamic Casimir force measurements. G. Jourdan, A. Lambrecht, F. Comin, J. Chevrier : Submitted PRL 2007.

Kinetic Roughening of charge spreading in a two-dimensional silicon nanocrystal network detected by electrostatic force microscopy. R. Dianoux, H.J.H. Smilde, F. Marchi, N. Buffet, P. Mur, F. Comin, J. Chevrier Phys. Rev. B 71, 125303 (2005).

XPS and AFM investigation of hafnium dioxide thin films prepared by atomic layer deposition on silicon. V. Sammelselg, R. Rammula, J. Aarik, A. Kikas, K. Kooser and T. Käämbre. Journal of Electron Spectroscopy and Related Phenomena, 156–158 (2007).

*Effect of phase composition on X-ray absorption spectra of ZrO_2 thin films.*A. Kikas, J. Aarik, V. Kisand, K. Kooser, T. Käämbre, H. Mändar T. Uustare, R. Rammula, V. Sammelselg and I. Martinson. J. of El. Spect. and Related Phenomena, 156–158 (2007) 303–306.

Presence to International conferences

- International Baltic Sea Region Conference “Functional Materials and Nanotechnologies” (FM&NT-2007). Riga, Latvia, April 2-4, 2007
- E-MRS Fall Meeting 2007, Symposium J: Microscopy and spectroscopy techniques in advanced materials characterization: Warsaw University of Technology, September 17-21, 2007 - Warsaw, Poland.
- The COE international symposium “Atomistic Fabrication Technology”, Icho-Kaikan, Osaka University, Suita, Osaka, Japan, October 15-17, 2007.
- Baltic conference on Atomic Layer Deposition (BALD 2006), June 19 - 20, 2006, Oslo, Norway — invited Talk.
- 10th International Conference on Electronic Spectroscopy and Structure (ICESS-10), August 28 – September 01 2006, Foz do Iguaçu, Brazil — Talk and Poster.
- ECOSS-24, September 04 - 07, 2006, Paris, France — Poster.
- SRI 2006 - The Ninth International Conference on Synchrotron Radiation Instrumentation May 28 - June 3, 2006, EXCO Center, Daegu, Korea — Talk
- MRS Fall Meeting, November 28 - December 2, 2005, Boston, MA, USA — Talk
- ICN+T 06, International Conference on Nanoscience and Technology NANO9 meets STM’06, July 30–August 4, 2006, Basel, Switzerland — Talk
- Workshop on the Coupling of Synchrotron Radiation IR and X-rays with Tip based Scanning Probe Microscopies; ESRF November 16th – 18th 2005.
- MMD 05, International Conference on Matter Materials and Devices, June 22th-25th, 2005, Genova, Italy.
- 18th International Conference on X-ray Optics and Microanalysis "ICXOM 2005" Frascati (Rome- Italy), 25-30 September 2005.

Presentations and participations to Workshop and Conferences
(and related Conference Proceedings)

18th International Conference on X-ray Optics and Microanalysis "ICXOM 2005"
Frascati (Rome- Italy), 25-30 September 2005.
Oral Communication (J. Purans):
Element-Specific Contrast in Local Probe Microscopy via X-ray Spectroscopy: Present Status and Future Perspectives.

1° workshop « Nanoparticle’s Spectroscopy with Synchrotron Radiation », Organized by SILS (Italian Society of Synchrotron Radiation). Gargnano (BS), 2-3 March 2006.
Oral Communication (S. Larcheri):
Nano-XEOL in near-field detection.
Larcheri S. Armellini C. Rocca F., Pailharey D., Mathey Y., Jandard F., Dalba G. , Graziola R., Grisenti R., Fornasini P., Dhez O., Kuzmin A., Kalendarev R., Purans J., and Sammelselg V.

SILS 2006 - XIV Convegno della Società Italiana di Luce di Sincrotrone.
Napoli- Italy, 6 -8 July 2006.
Poster presentation:
Nano-XEOL in near-field detection: first experimental results.
Larcheri S. Armellini C. Rocca F., Pailharey D., Mathey Y., Jandard F., Dalba G. , Graziola R., Grisenti R., Fornasini P., Dhez O., Kuzmin A., Kalendarev R., Purans J., and Sammelselg V.

Workshop “NanoMetrology 2007: Metrology for Nanotechnology”, Organized by INRIM

(National Institute of Metrological Research), Torino – Italy. Torino – Italy, 14-15 June 2007.
Poster presentation:
A new microscope for combined SNOM and X-ray absorption measurements
S. Larcheri, F. Rocca, D. Pailharey, F. Jandard, G. Dalba, R. Graziola, A. Kuzmin and J. Purans

International Baltic Sea Region Conference "Functional Materials and Nanotechnologies" (FM&NT-2007). Riga, Latvia, April 2-4, 2007:

Oral presentation (A. Kuzmin):
Nano-scale X-ray absorption spectroscopy using XEOL-SNOM detection mode.
D.Pailharey, Y.Mathey, F.Jandard, S.Larcheri, F.Rocca, A.Kuzmin, R.Kalendarev, J.Purans, G.Dalba, R.Graziola, O.Dhez,
Journal of Physics: Conference Series **93** (2007) 012038

Poster presentation:
Zn K-edge XANES in nanocrystalline ZnO.
A.Kuzmin, S.Larcheri and F.Rocca.
Journal of Physics: Conference Series **93** (2007) 012045

Poster presentation:
Patterned test samples for scanning near field optical microscope by electron beam lithography.
R.Krutohvostov, A.Kuzmin, R.Kalendarev, V.Zauls,
Paper accepted for publication in Journal of Physics: Conference Series.

The E-MRS Fall Meeting 2007,
Symposium J: Microscopy and spectroscopy techniques in advanced materials characterization: Warsaw University of Technology, September 17-21, 2007- Warsaw, Poland.

Oral Communication (S. Larcheri):
A new tool for nano-scale X-ray absorption spectroscopy and element-specific SNOM microscopy. S. Larcheri, F. Rocca, D. Pailharey, F. Jandard, R. Graziola, G. Dalba, A. Kuzmin, R. Kalendarev and J. Purans. Paper submitted for publication in the Proceedings.

The COE international symposium "Atomistic Fabrication Technology",
Icho-Kaikan, Osaka University, Suita, Osaka, Japan, October 15-17, 2007.

Invited talk (J. Purans):
Near field X-ray spectromicroscopies: new tools for nanoscience

XI ANNEXES

- Leaflet for the BL AFM manufactured by “Small Infinity”.
- Documents relevant to the company Small Infinity (from the application for a national grant for innovation OSEO-ANVAR).
- Extract from the Ph.D. Thesis of Silvia Larcheri (Uni. of Trento, Italy).

Leaflet for the BL AFM

Small Infinity

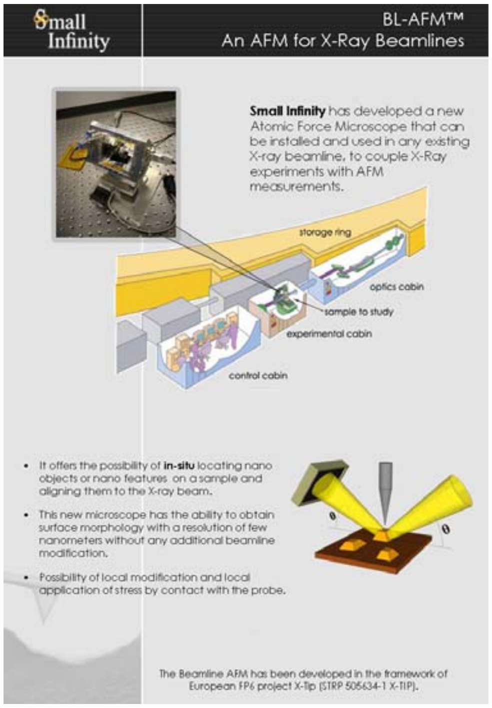
Bring light into your nanoworld

X-RAY

Beamline AFM

Michal Hrouzek

12/12/2007



Small Infinity

BL-AFM™
An AFM for X-Ray Beamlines

Small Infinity has developed a new Atomic Force Microscope that can be installed and used in any existing X-ray beamline, to couple X-Ray experiments with AFM measurements.

- It offers the possibility of **in-situ** locating nano objects or nano features on a sample and aligning them to the X-ray beam.
- This new microscope has the ability to obtain surface morphology with a resolution of few nanometers without any additional beamline modification.
- Possibility of local modification and local application of stress by contact with the probe.

The Beamline AFM has been developed in the framework of European FP6 project X-Tip (STRP 505634-1 X-TIP).

Designed by
Synchrotron experts

X-RAY

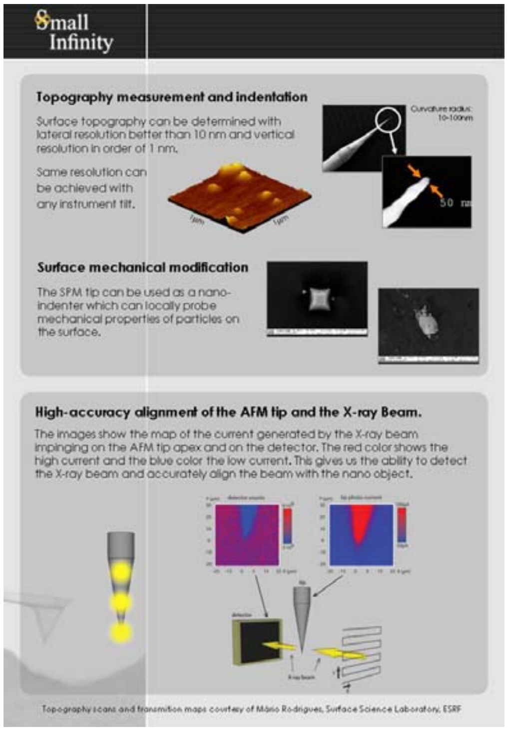
ESRF

Small Infinity is a spin-off of the **European Synchrotron Radiation Facility** (ESRF) specialized in the development and production of Scanning Probe Microscopes.

- The technology developed is the result of a research program performed in the Surface Science Laboratory (SSL).
- The SSL focuses on the use of Scanning Probe Microscopy (SPM) for supplementing synchrotron radiation techniques in issues relevant to nanotechnology.
- The results obtained open new possibilities to combine SPM with synchrotron radiation.

Advantages:

- Easy implementation on the end station.
- Robustness to mechanical and electromagnetic perturbations
- Sample topography measurement.
- Ability to measure strongly-curved surfaces.
- Nano structure and X-ray beam localization.
- Nano structure alignment with the X-ray beam.
- Possibility of mechanical modification of the sample.
- Local application of mechanical stress.
- Local photon and/or electron detection.
- Local X-ray scattering detection.



Small Infinity

Topography measurement and indentation

Surface topography can be determined with lateral resolution better than 10 nm and vertical resolution in order of 1 nm.

Same resolution can be achieved with any instrument tilt.

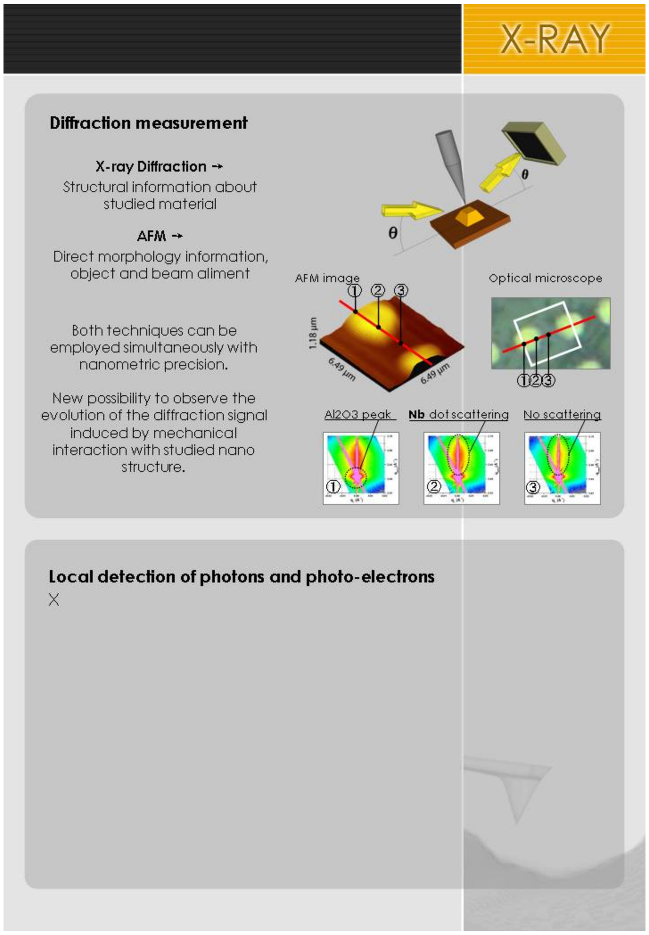
Surface mechanical modification

The SPM tip can be used as a nano-indenter which can locally probe mechanical properties of particles on the surface.

High-accuracy alignment of the AFM tip and the X-ray Beam.

The images show the map of the current generated by the X-ray beam impinging on the AFM tip apex and on the detector. The red color shows the high current and the blue color the low current. This gives us the ability to detect the X-ray beam and accurately align the beam with the nano object.

Topography scans and transmition maps courtesy of Mário Rodrigues, Surface Science Laboratory, ESRF



Diffraction measurement

X-ray Diffraction →
Structural information about studied material

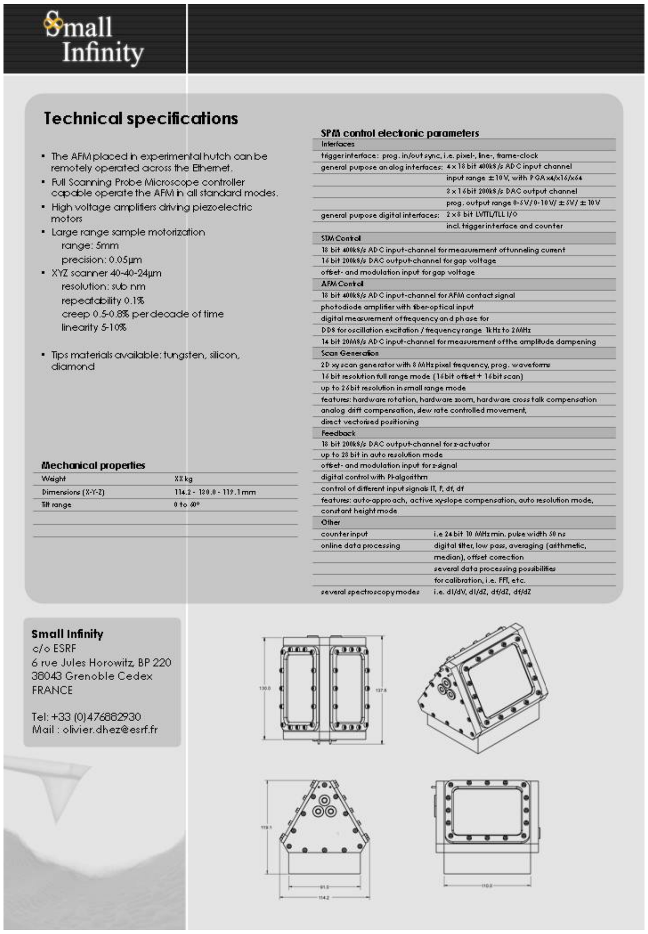
AFM →
Direct morphology information, object and beam aliment

Both techniques can be employed simultaneously with nanometric precision.

New possibility to observe the evolution of the diffraction signal induced by mechanical interaction with studied nano structure.

Local detection of photons and photo-electrons

X



Technical specifications

- The AFM placed in experimental hutch can be remotely operated across the Ethernet.
- Full Scanning Probe Microscope controller capable operate the AFM in all standard modes.
- High voltage amplifiers driving piezoelectric motors
- Large range sample motorization
  range: 5mm
  precision: 0.05µm
- XYZ scanner 40-40-24µm
  resolution: sub nm
  repeatability 0.1%
  creep 0.5-0.8% per decade of time
  linearity 5-10%
- Tips materials available: tungsten, silicon, diamond

Mechanical properties

Weight	XX kg
Dimensions (X-Y-Z)	114.2 - 130.0 - 119.1 mm
Tilt range	0 to 60°

SPM control electronic parameters

Interfaces	
trigger interface: prog. in/out sync, i.e. pixel-, line-, frame-clock	
general purpose analog interfaces:	4 × 18 bit 400kS/s ADC input channel
	input range ±10V, with PGA x4/x16/x64
	3 × 16 bit 200kS/s DAC output channel
	prog. output range 0-5V/0-10V/±5V/±10V
general purpose digital interfaces:	2 × 8 bit LVTTL/TLL I/O
	incl. trigger interface and counter
STM Control	
18 bit 400kS/s ADC input-channel for measurement of tunneling current	
16 bit 200kS/s DAC output-channel for gap voltage	
offset- and modulation input for gap voltage	
AFM Control	
18 bit 400kS/s ADC input-channel for AFM contact signal	
photodiode amplifier with fiber-optical input	
digital measurement of frequency and phase for	
DDS for oscillation excitation / frequency range 1kHz to 2MHz	
14 bit 20MS/s ADC input-channel for measurement of the amplitude dampening	
Scan Generation	
2D xy scan generator with 8 MHz pixel frequency, prog. waveforms	
16 bit resolution full range mode (16bit offset + 16bit scan)	
up to 26bit resolution in small range mode	
features: hardware rotation, hardware zoom, hardware cross talk compensation	
analog drift compensation, slew rate controlled movement,	
direct vectorised positioning	
Feedback	
18 bit 200kS/s DAC output-channel for z-actuator	
up to 28 bit in auto resolution mode	
offset- and modulation input for z-signal	
digital control with PI-algorithm	
control of different input signals IT, F, df, df	
features: auto-approach, active xy-slope compensation, auto resolution mode,	
constant height mode	
Other	
counter input	i.e 24 bit 10 MHz min. pulse width 50 ns
online data processing	digital filter, low pass, averaging (arithmetic,
	median), offset correction
	several data processing possibilities
	for calibration, i.e. FFT, etc.
several spectroscopy modes	i.e. dI/dV, dI/dZ, df/dZ, df/dZ

Small Infinity
c/o ESRF
6 rue Jules Horowitz, BP 220
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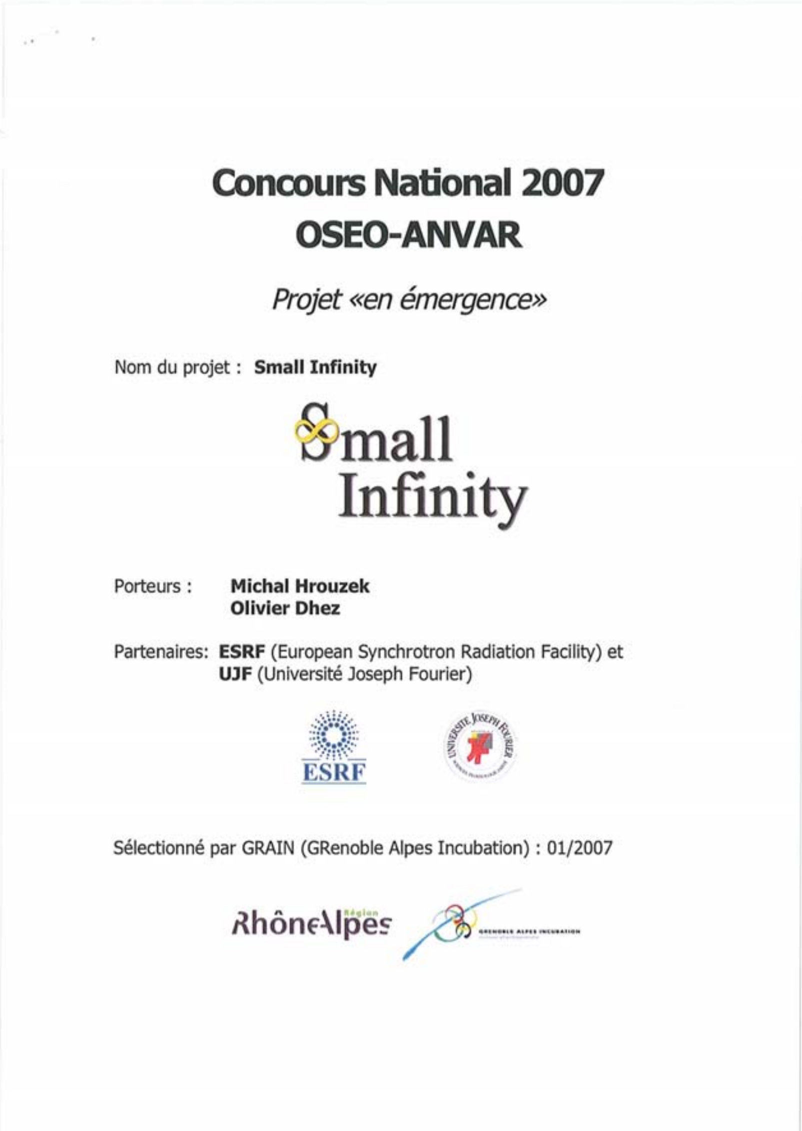


Concours National 2007
OSEO-ANVAR

Projet «en émergence»

Nom du projet : **Small Infinity**

Small Infinity

Porteurs : **Michal Hrouzek**
Olivier Dhez

Partenaires: **ESRF** (European Synchrotron Radiation Facility) et
UJF (Université Joseph Fourier)

Sélectionné par GRAIN (GRenoble Alpes Incubation) : 01/2007

Concours National 2007 Projet « en émergence »

1. DESCRIPTION DU PROJET

- ***Origine du projet***

Suite à l'expertise acquise au cours du projet européen X-Tip (STRP 505634-1 X-TIP) dans la construction de microscope à force atomique (AFM) couplé avec le rayonnement synchrotron, à la prise du brevet (Nº 06/04674) pour un nouveau mode de fonctionnement pour les microscopes à force atomique (AFM) et à l'expertise dans le contrôle de nano positionnement, ainsi que la demande du marché, nous avons décidé de commencer ce processus de valorisation. La figure 1 présente le principe de fonctionnement d'un microscope AFM. Une pointe de taille micrométrique est déplacée sur la surface à caractériser, dont le déplacement vertical est enregistré grâce au laser réfléchi sur celle-ci.

Figure 1 : *Schéma de principe de fonctionnement d'un microscope a force atomique*

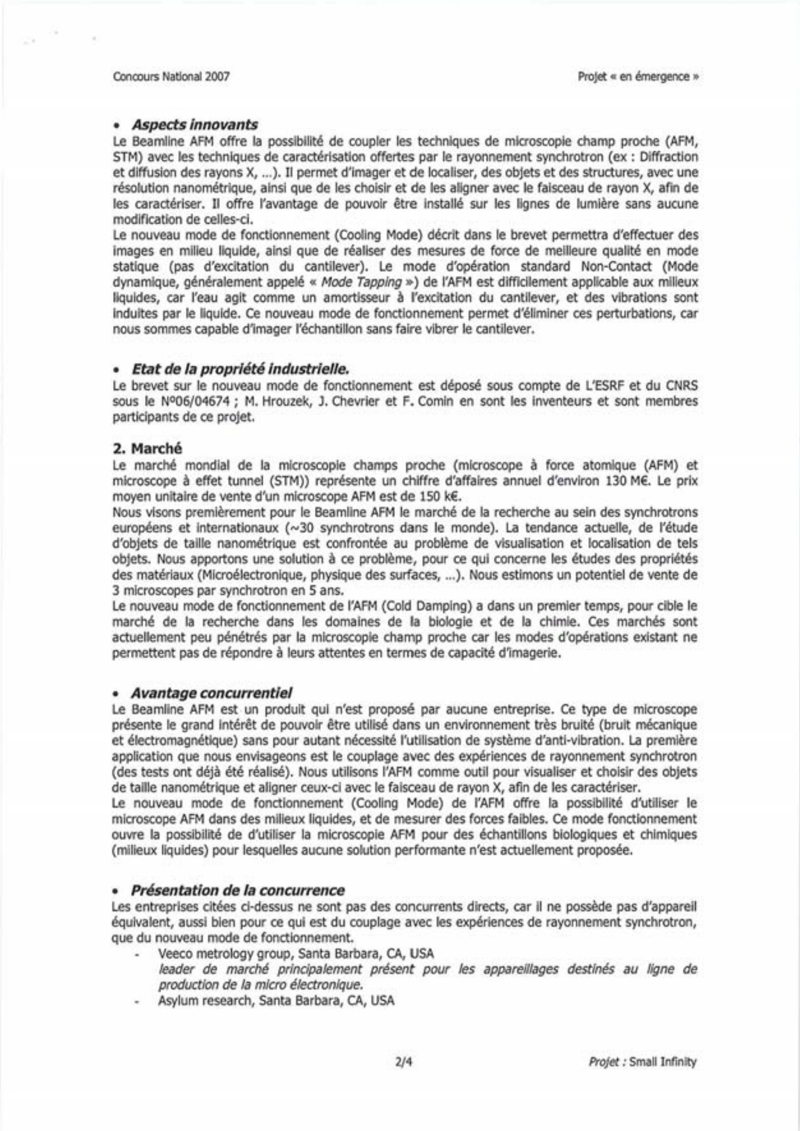
- ***Description du produit***

Le projet comprend le développement de 3 produits et d'une activité de service dans le domaine de la microscopie à force atomique (AFM).
Le premier produit est un microscope AFM spécialisé pour être installé sur les lignes de lumière qui utilisent le rayonnement synchrotron, appelé « *Beamline AFM* » ou « *BL-AFM* » (voir Figure 2). Un prototype déjà existant a permis de montrer la preuve de concept, et son intérêt pour la location et le positionnement d'objet de taille nanométrique, afin de permettre leurs études avec le rayonnement synchrotron. Grâce à son design ce microscope offre ainsi la possibilité d'effectuer des études de surface pour des échantillons de forme complexe (ex. miroirs fortement concave, …)
Les deux autres produits sont des microscopes AFM dans lesquels sera intégré le nouveau mode de fonctionnement basé sur le brevet. La figure 3 montre un dessin de la tête active du prototype existant. Un microscope est destiné aux applications pour des échantillons de type surface « *sèche* », et un deuxième appliqué aux échantillons en milieux liquides. Un prototype de laboratoire basé sur la modification d'un appareil commercial est actuellement utilisé pour démontrer la preuve de concept et la validation de ce nouveau mode de fonctionnement.
Finalement nous souhaitons développer une activité de service de caractérisation de surface utilisant les spécificités offertes par ces microscopes.

Figure 2 : *Photos du prototype de microscope adapté pour l'utilisation avec le rayonnement synchrotron*

Figure 3 : *Design de la tête active pour la mise en œuvre du nouveau mode fonctionnement du microscope AFM.*

1/4 *Projet :* Small Infinity



- ***Aspects innovants***

Le Beamline AFM offre la possibilité de coupler les techniques de microscopie champ proche (AFM, STM) avec les techniques de caractérisation offertes par le rayonnement synchrotron (ex : Diffraction et diffusion des rayons X, …). Il permet d'imager et de localiser, des objets et des structures, avec une résolution nanométrique, ainsi que de les choisir et de les aligner avec le faisceau de rayon X, afin de les caractériser. Il offre l'avantage de pouvoir être installé sur les lignes de lumière sans aucune modification de celles-ci.
Le nouveau mode de fonctionnement (Cooling Mode) décrit dans le brevet permettra d'effectuer des images en milieu liquide, ainsi que de réaliser des mesures de force de meilleure qualité en mode statique (pas d'excitation du cantilever). Le mode d'opération standard Non-Contact (Mode dynamique, généralement appelé « *Mode Tapping* ») de l'AFM est difficilement applicable aux milieux liquides, car l'eau agit comme un amortisseur à l'excitation du cantilever, et des vibrations sont induites par le liquide. Ce nouveau mode de fonctionnement permet d'éliminer ces perturbations, car nous sommes capable d'imager l'échantillon sans faire vibrer le cantilever.

- ***Etat de la propriété industrielle.***

Le brevet sur le nouveau mode de fonctionnement est déposé sous compte de L'ESRF et du CNRS sous le N°06/04674 ; M. Hrouzek, J. Chevrier et F. Comin en sont les inventeurs et sont membres participants de ce projet.

2. Marché

Le marché mondial de la microscopie champs proche (microscope à force atomique (AFM) et microscope à effet tunnel (STM)) représente un chiffre d'affaires annuel d'environ 130 M€. Le prix moyen unitaire de vente d'un microscope AFM est de 150 k€.
Nous visons premièrement pour le Beamline AFM le marché de la recherche au sein des synchrotrons européens et internationaux (~30 synchrotrons dans le monde). La tendance actuelle, de l'étude d'objets de taille nanométrique est confrontée au problème de visualisation et localisation de tels objets. Nous apportons une solution à ce problème, pour ce qui concerne les études des propriétés des matériaux (Microélectronique, physique des surfaces, …). Nous estimons un potentiel de vente de 3 microscopes par synchrotron en 5 ans.
Le nouveau mode de fonctionnement de l'AFM (Cold Damping) a dans un premier temps, pour cible le marché de la recherche dans les domaines de la biologie et de la chimie. Ces marchés sont actuellement peu pénétrés par la microscopie champ proche car les modes d'opérations existant ne permettent pas de répondre à leurs attentes en termes de capacité d'imagerie.

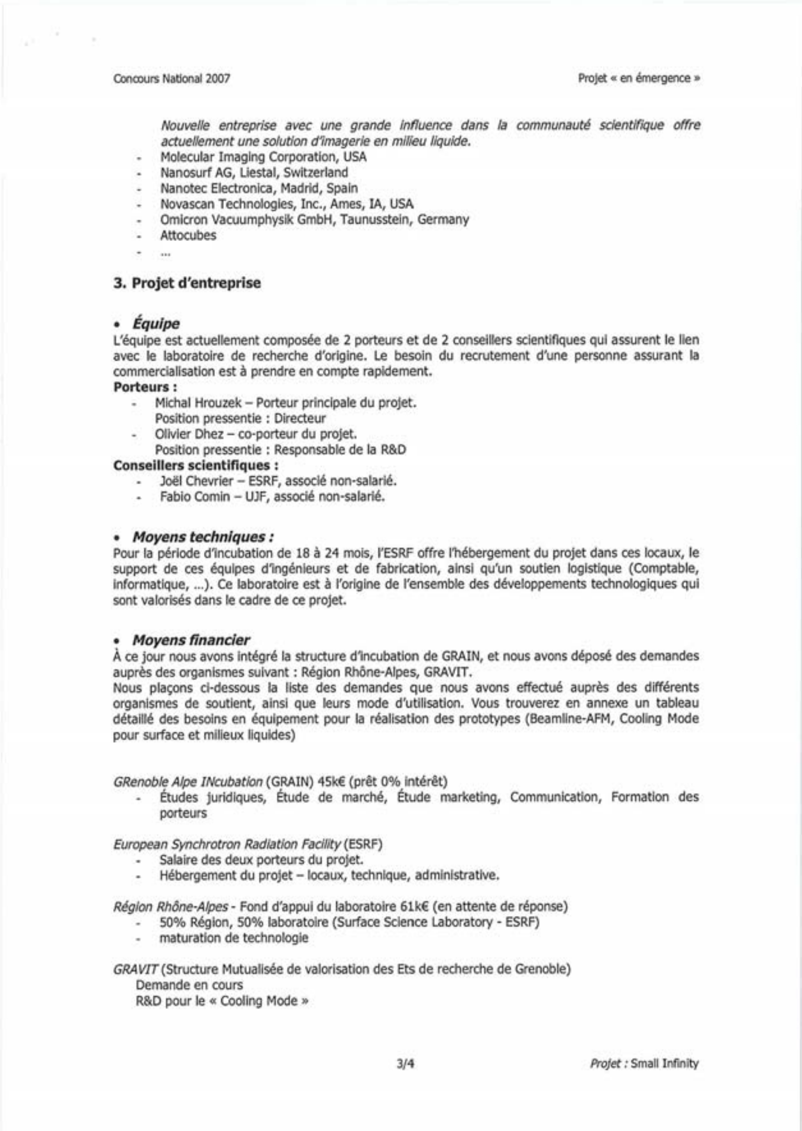
- ***Avantage concurrentiel***

Le Beamline AFM est un produit qui n'est proposé par aucune entreprise. Ce type de microscope présente le grand intérêt de pouvoir être utilisé dans un environnement très bruité (bruit mécanique et électromagnétique) sans pour autant nécessité l'utilisation de système d'anti-vibration. La première application que nous envisageons est le couplage avec des expériences de rayonnement synchrotron (des tests ont déjà été réalisé). Nous utilisons l'AFM comme outil pour visualiser et choisir des objets de taille nanométrique et aligner ceux-ci avec le faisceau de rayon X, afin de les caractériser.
Le nouveau mode de fonctionnement (Cooling Mode) de l'AFM offre la possibilité d'utiliser le microscope AFM dans des milieux liquides, et de mesurer des forces faibles. Ce mode fonctionnement ouvre la possibilité de d'utiliser la microscopie AFM pour des échantillons biologiques et chimiques (milieux liquides) pour lesquelles aucune solution performante n'est actuellement proposée.

- ***Présentation de la concurrence***

Les entreprises citées ci-dessus ne sont pas des concurrents directs, car il ne possède pas d'appareil équivalent, aussi bien pour ce qui est du couplage avec les expériences de rayonnement synchrotron, que du nouveau mode de fonctionnement.

- Veeco metrology group, Santa Barbara, CA, USA
  leader de marché principalement présent pour les appareillages destinés au ligne de production de la micro électronique.
- Asylum research, Santa Barbara, CA, USA



Nouvelle entreprise avec une grande influence dans la communauté scientifique offre actuellement une solution d'imagerie en milieu liquide.

- Molecular Imaging Corporation, USA
- Nanosurf AG, Liestal, Switzerland
- Nanotec Electronica, Madrid, Spain
- Novascan Technologies, Inc., Ames, IA, USA
- Omicron Vacuumphysik GmbH, Taunusstein, Germany
- Attocubes
- …

3. Projet d'entreprise

- ***Équipe***

L'équipe est actuellement composée de 2 porteurs et de 2 conseillers scientifiques qui assurent le lien avec le laboratoire de recherche d'origine. Le besoin du recrutement d'une personne assurant la commercialisation est à prendre en compte rapidement.

Porteurs :

- Michal Hrouzek – Porteur principale du projet.
  Position pressentie : Directeur
- Olivier Dhez – co-porteur du projet.
  Position pressentie : Responsable de la R&D

Conseillers scientifiques :

- Joël Chevrier – ESRF, associé non-salarié.
- Fabio Comin – UJF, associé non-salarié.

- ***Moyens techniques :***

Pour la période d'incubation de 18 à 24 mois, l'ESRF offre l'hébergement du projet dans ces locaux, le support de ces équipes d'ingénieurs et de fabrication, ainsi qu'un soutien logistique (Comptable, informatique, …). Ce laboratoire est à l'origine de l'ensemble des développements technologiques qui sont valorisés dans le cadre de ce projet.

- ***Moyens financier***

À ce jour nous avons intégré la structure d'incubation de GRAIN, et nous avons déposé des demandes auprès des organismes suivant : Région Rhône-Alpes, GRAVIT.
Nous plaçons ci-dessous la liste des demandes que nous avons effectué auprès des différents organismes de soutient, ainsi que leurs mode d'utilisation. Vous trouverez en annexe un tableau détaillé des besoins en équipement pour la réalisation des prototypes (Beamline-AFM, Cooling Mode pour surface et milieux liquides)

GRenoble Alpe INcubation (GRAIN) 45k€ (prêt 0% intérêt)

- Études juridiques, Étude de marché, Étude marketing, Communication, Formation des porteurs

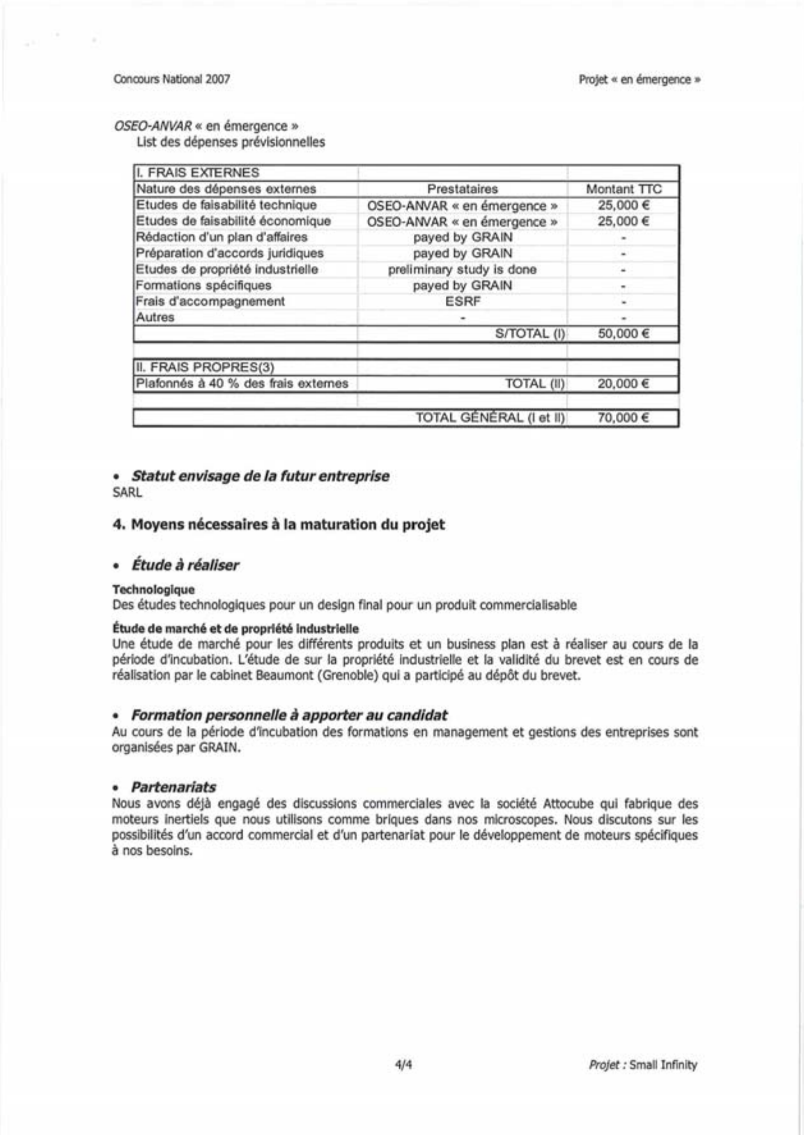
European Synchrotron Radiation Facility (ESRF)

- Salaire des deux porteurs du projet.
- Hébergement du projet – locaux, technique, administrative.

Région Rhône-Alpes - Fond d'appui du laboratoire 61k€ (en attente de réponse)

- 50% Région, 50% laboratoire (Surface Science Laboratory - ESRF)
- maturation de technologie

GRAVIT (Structure Mutualisée de valorisation des Ets de recherche de Grenoble)
Demande en cours
R&D pour le « Cooling Mode »



OSEO-ANVAR « en émergence »
List des dépenses prévisionnelles

I. FRAIS EXTERNES		
Nature des dépenses externes	Prestataires	Montant TTC
Etudes de faisabilité technique	OSEO-ANVAR « en émergence »	25,000 €
Etudes de faisabilité économique	OSEO-ANVAR « en émergence »	25,000 €
Rédaction d'un plan d'affaires	payed by GRAIN	-
Préparation d'accords juridiques	payed by GRAIN	-
Etudes de propriété industrielle	preliminary study is done	-
Formations spécifiques	payed by GRAIN	-
Frais d'accompagnement	ESRF	-
Autres	-	-
	S/TOTAL (I)	50,000 €
II. FRAIS PROPRES(3)		
Plafonnés à 40 % des frais externes	TOTAL (II)	20,000 €
	TOTAL GÉNÉRAL (I et II)	70,000 €

- ***Statut envisage de la futur entreprise***

SARL

4. Moyens nécessaires à la maturation du projet

- ***Étude à réaliser***

Technologique
Des études technologiques pour un design final pour un produit commercialisable

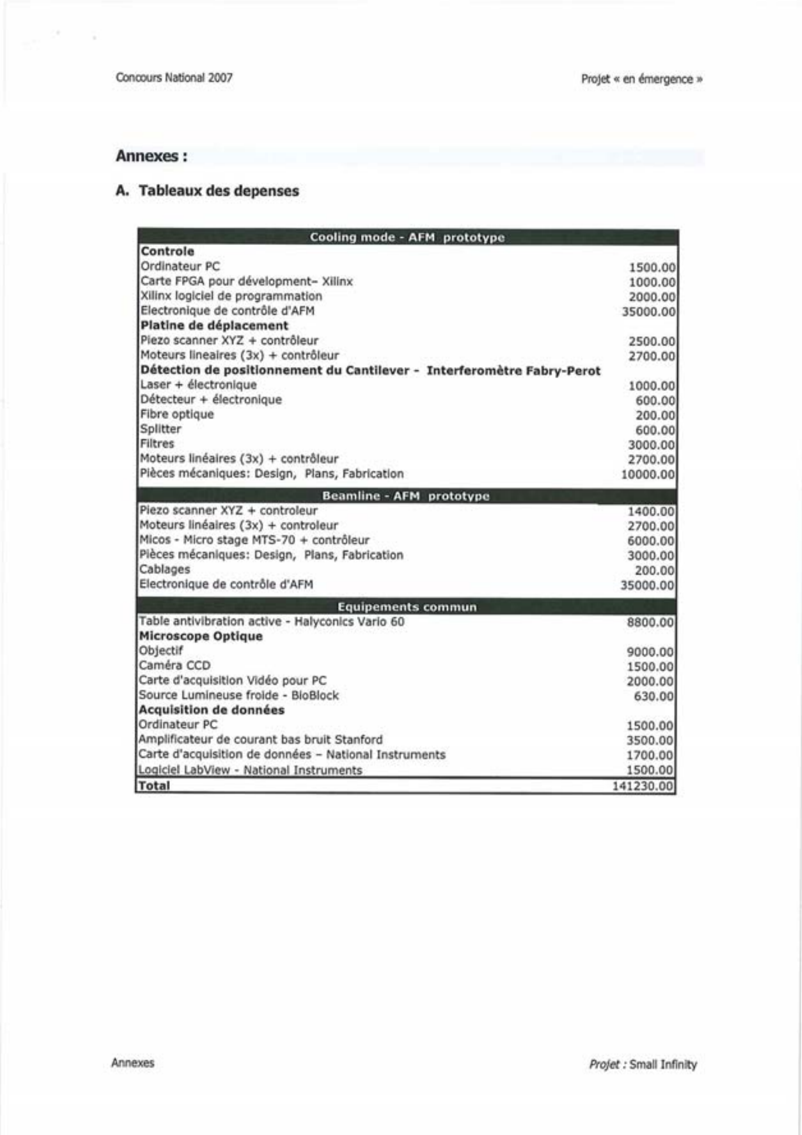
Étude de marché et de propriété industrielle
Une étude de marché pour les différents produits et un business plan est à réaliser au cours de la période d'incubation. L'étude de sur la propriété industrielle et la validité du brevet est en cours de réalisation par le cabinet Beaumont (Grenoble) qui a participé au dépôt du brevet.

- ***Formation personnelle à apporter au candidat***

Au cours de la période d'incubation des formations en management et gestions des entreprises sont organisées par GRAIN.

- ***Partenariats***

Nous avons déjà engagé des discussions commerciales avec la société Attocube qui fabrique des moteurs inertiels que nous utilisons comme briques dans nos microscopes. Nous discutons sur les possibilités d'un accord commercial et d'un partenariat pour le développement de moteurs spécifiques à nos besoins.



Annexes :

A. Tableaux des depenses

Cooling mode - AFM prototype	
Controle	
Ordinateur PC	1500.00
Carte FPGA pour dévelopment- Xilinx	1000.00
Xilinx logiciel de programmation	2000.00
Electronique de contrôle d'AFM	35000.00
Platine de déplacement	
Piezo scanner XYZ + contrôleur	2500.00
Moteurs lineaires (3x) + contrôleur	2700.00
Détection de positionnement du Cantilever - Interferomètre Fabry-Perot	
Laser + électronique	1000.00
Détecteur + électronique	600.00
Fibre optique	200.00
Splitter	600.00
Filtres	3000.00
Moteurs linéaires (3x) + contrôleur	2700.00
Pièces mécaniques: Design, Plans, Fabrication	10000.00
Beamline - AFM prototype	
Piezo scanner XYZ + controleur	1400.00
Moteurs linéaires (3x) + controleur	2700.00
Micos - Micro stage MTS-70 + contrôleur	6000.00
Pièces mécaniques: Design, Plans, Fabrication	3000.00
Cablages	200.00
Electronique de contrôle d'AFM	35000.00
Equipements commun	
Table antivibration active - Halyconics Vario 60	8800.00
Microscope Optique	
Objectif	9000.00
Caméra CCD	1500.00
Carte d'acquisition Vidéo pour PC	2000.00
Source Lumineuse froide - BioBlock	630.00
Acquisition de données	
Ordinateur PC	1500.00
Amplificateur de courant bas bruit Stanford	3500.00
Carte d'acquisition de données – National Instruments	1700.00
Logiciel LabView - National Instruments	1500.00
Total	141230.00

UNIVERSITA' DEGLI STUDI DI TRENTO

Facoltà di Scienze Matematiche Fisiche e Naturali

Joint use of x-ray synchrotron radiation microbeams and tip assisted photon detection for nano-scale XAFS spectroscopy and chemically sensitive surface mapping

Ph.D. student: **Silvia Larcheri**

Supervisors: **prof. G. Dalba and dr. F. Rocca**

Extract from the PhD thesis by Silvia Larcheri.

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Ph.D. Thesis in Physics, XIX cycle

February 2007

Abstract

The thesis research activity has been focused on the development of the XAS-SNOM microscope device and related technique. The work concerned the photon detection, namely the local collection of the x-ray excited optical luminescence (XEOL) by means of the optical fiber probe of a scanning near field optical microscope (SNOM), operating in shear-force mode. The final aim was to record the simultaneous topographical and optical imaging of the sample surface and to perform local x-ray absorption fine structure (XAFS) measurements at a fixed point of the sample surface in XEOL detection mode.

Chapter 1 opens the thesis with a detailed description of the X-TIP project, focusing in particular on its purposes and on the technological relevance of this project within the current scientific panorama. The second part of the chapter introduces the specific issues of interest to the thesis, i.e. the photon detection work package. The SNOM and XAFS-XEOL investigation techniques employed for photon detection are presented in **chapter 2**. Since a thorough survey of the theoretical foundations of SNOM and XAFS-XEOL goes beyond the aim of this work, this chapter mainly focuses on the specificities and current experimental applications of these techniques. In **chapter 3** all components of the XAS-SNOM instrumentation as it looks in its final, improved version are in turn described: the microscope head, the XEOL detection setup and the optical fiber probes employed to collect the optical signal. A last paragraph examines the spatial resolution characterization tests carried out on the XAS-SNOM prototype device at the CRMC-N Laboratories in Marseille. Since ZnO nanostructured materials have been selected as good candidates for simultaneous SNOM and XAFS-XEOL investigations, **chapter 4** offers a brief overview of properties and scientific findings available in literature on this compound. However, the most important part of this chapter presents the ZnO thin films *ad hoc* prepared for the X-TIP project, pointing out mainly the growth techniques and structural and optical characterization studies performed on each sample. **Chapter 5** covers all issues related to the XAS-SNOM device installation and experiment implementation at the European Synchrotron Radiation Facility (ESRF) in Grenoble. A detailed analysis of the major results obtained by means of the XTIP XAS-SNOM prototype is presented, namely the local collection of XEOL and XEOL-XANES spectra at a fixed point of the sample surface and the topographical and optical imaging obtained by scanning the fiber probe on the surface. A last chapter summarizes the most important findings achieved by the novel XAS-SNOM technique and experimental apparatus installed at ESRF. Besides drawing the conclusions, the major guidelines for the future research work will be traced, as regards both short and long-term perspectives.

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