Element-Specific Contrast in Local Probe Microscopy via X-Ray Spectroscopy: Present Status and Future Perspectives

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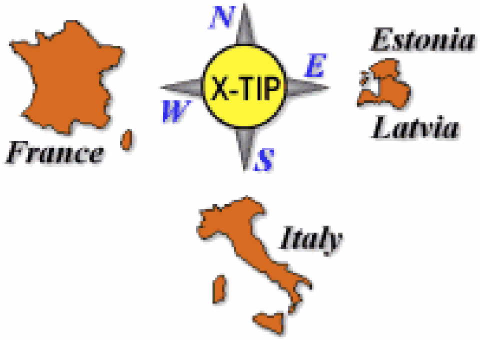

X-TIP

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

STRP 505634-1 X-TIP

Dr. F. Comin and beamline staffs at the ESRF
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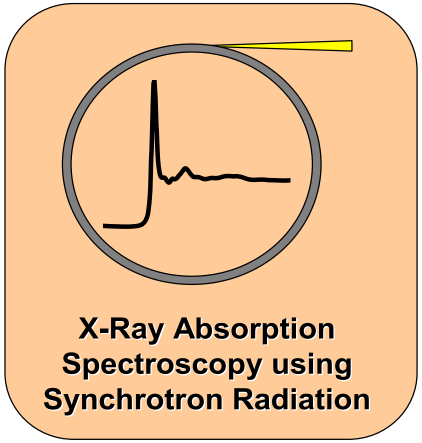
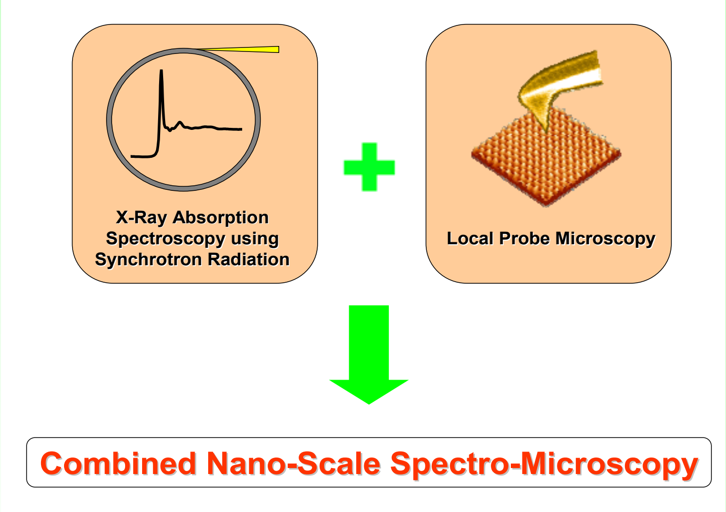
Prof. V. Sammelseg UNITA (Tatru, Estomia)

Scanning Probe Microscopies (SPM) are perhaps the most remarkable new surface sensitive techniques. As matter of facts, SPM has already made a huge impact in nanoscale materials science, but it is not element specific and is sensitive mostly to surface morphology. This is a serious problem, since many materials are inhomogeneous over local element composition.

On the other hand, X-ray absorption spectroscopy (XAS) techniques such as XANES (X-ray Near Edge Structure - Selective Electronic and Chemical Analysis) and EXAFS (Extended X-ray Absorption Fine Structure - Selective Structural Analysis) probe the electronic and structural properties of materials. The main limitation has been the lack of lateral and vertical resolution: the best hard X-ray micro-XANES or EXAFS spectroscopy averages over sample areas of the order of several square microns. This is a serious problem, since many materials properties are inhomogeneous over a much smaller scale.



The basics of this technique are circulating since years:



- The first observations by STM of core-level photoelectrons generated by X-ray illumination of the tip-surface region have been published by Tsuji, Hasegawa and co-workers (1997)
- Ishii (1999) has measured the capacitance XAS signal with a metal scanning probe electrode
- Different combinations of XAS and SPM as a local detector were proposed by Purans (2001): SNOM+XAS; …
- combination of XRF technique and LPM with a cantilever (with a hole of 50 nm) as a *collimator* of X-ray beam was proposed by T. Nagamura (2003)
- Detailed STM study under synchrotron-radiation (SR) soft X-ray illumination was performed by Matsushima et al. (2004)

Development of SPM+XAS=XTIP

The development of XTIP new instrumentation is feasible due to the enormous progresses in the SPM techniques as well as in the X-Ray Radiation focusing techiques: (i) SR sources (ii) laboratory sources with polycapillary optics that ensure detection of required experimental signal from strongly confined, nano-scaled regions.

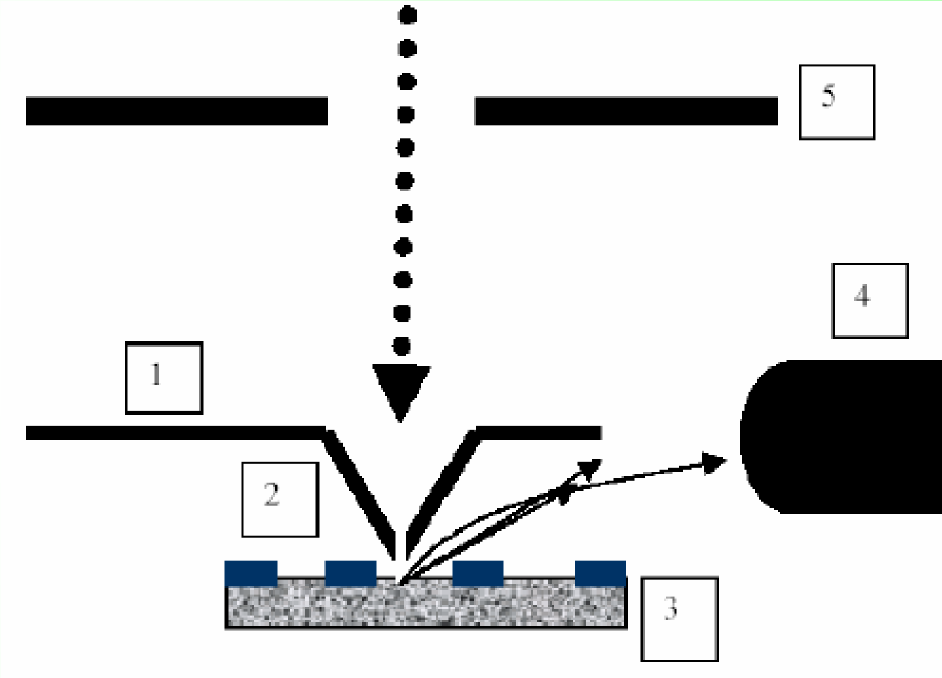
Two different ways will be explored :

•a cantilever (with the measurement hole of 50-100 nm) as a *collimator* of the focused X-ray beam on the cantilever;

•a cantilever as a *local probe detector* of the emission signals due to X-Ray processes in the sample.

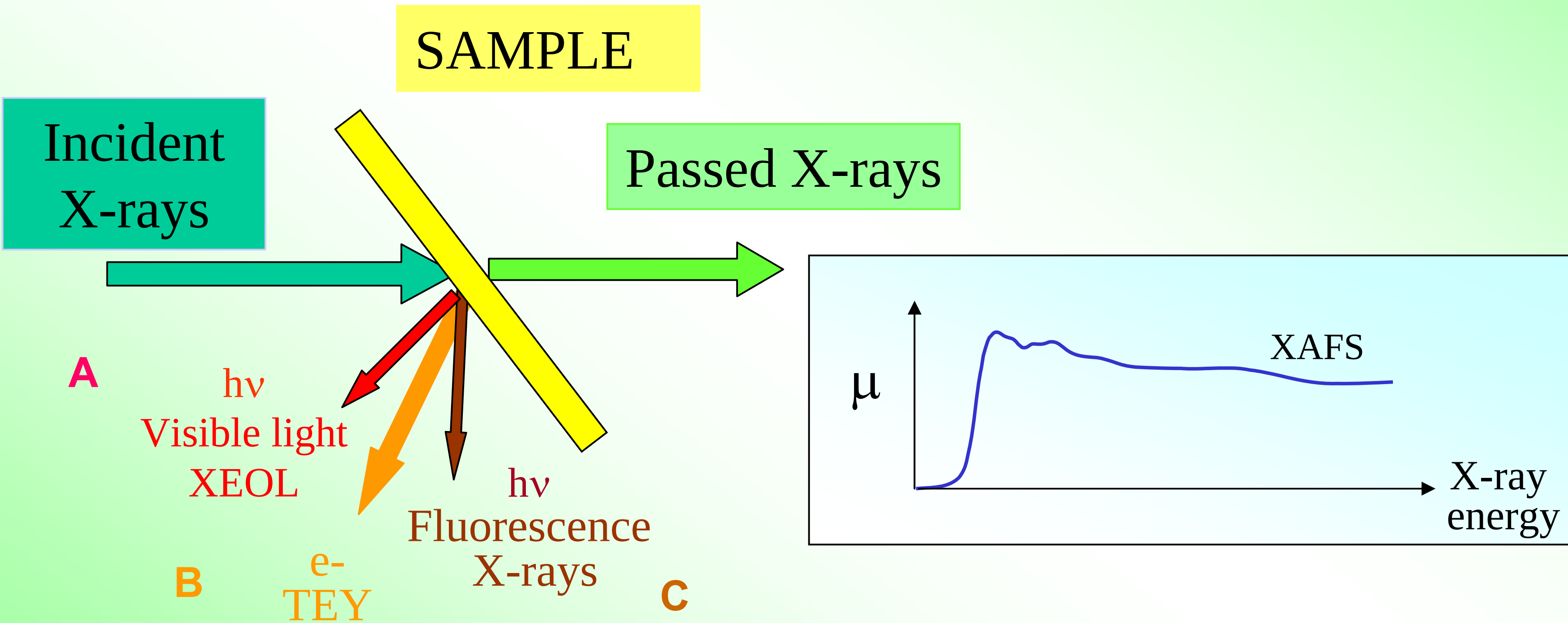
Nano-XRF, Nano-XEOL,…

The apparatus will include a scanning mechanism with a means of bringing a probe (1) in the vicinity of a sample (2); probe (1) - cantilever with the measurement hole of 50-100 nm; focused (5) on the hole X-ray micro-beam by Kumakhov Polycapillary Optics and “Laboratory Synchrotron”; (emission X-ray fluorescence) collection X-ray detector (4) (Si-PIN diode with energy resolution, and electronics controlling the instrument.



combination of XRF technique and LPM with a cantilever (with a hole of 50 nm) as a *collimator* of X-ray beam was proposed by T. Nagamura (2003)

XAFS measurements



A, B and C signals are able to be collected by a near field probe

Experiments based on far field A or B emissions have already been performed

J.K. Gimzewski, R. Berndt and R.R. Schlittler

Observation of local photoemission using a scanning tunneling microscope

Ultramicroscopy 42-44 (1992) 366-37

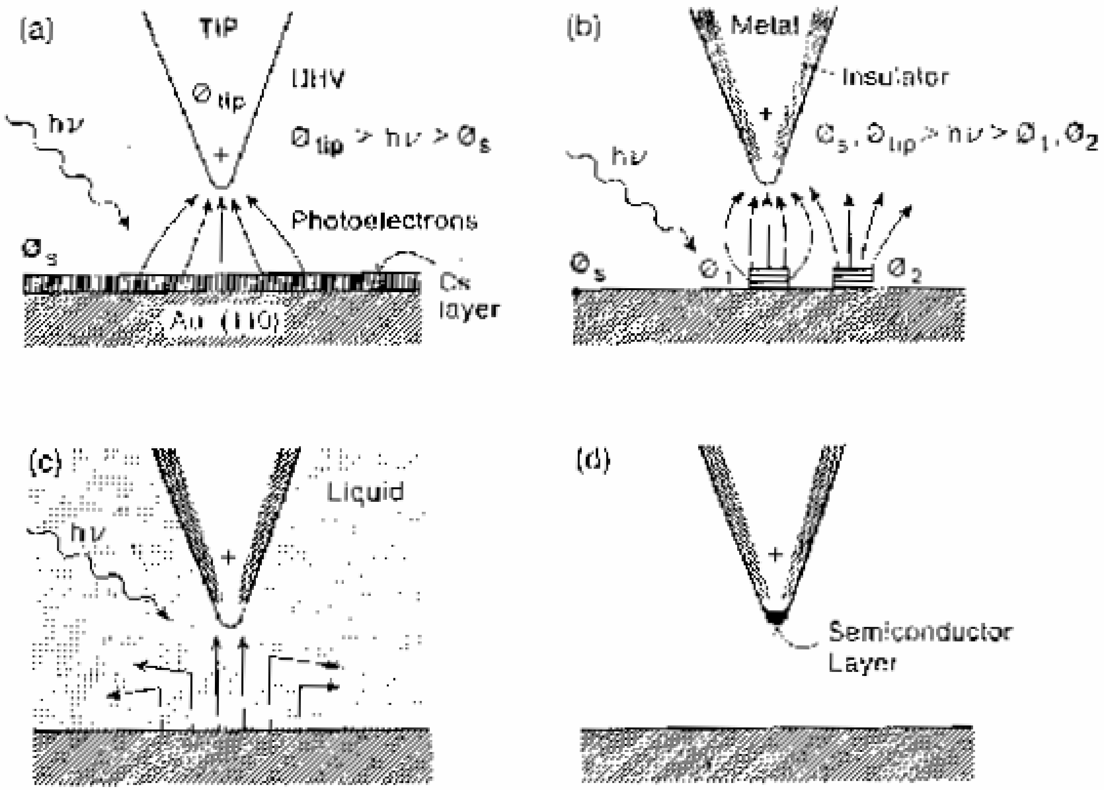
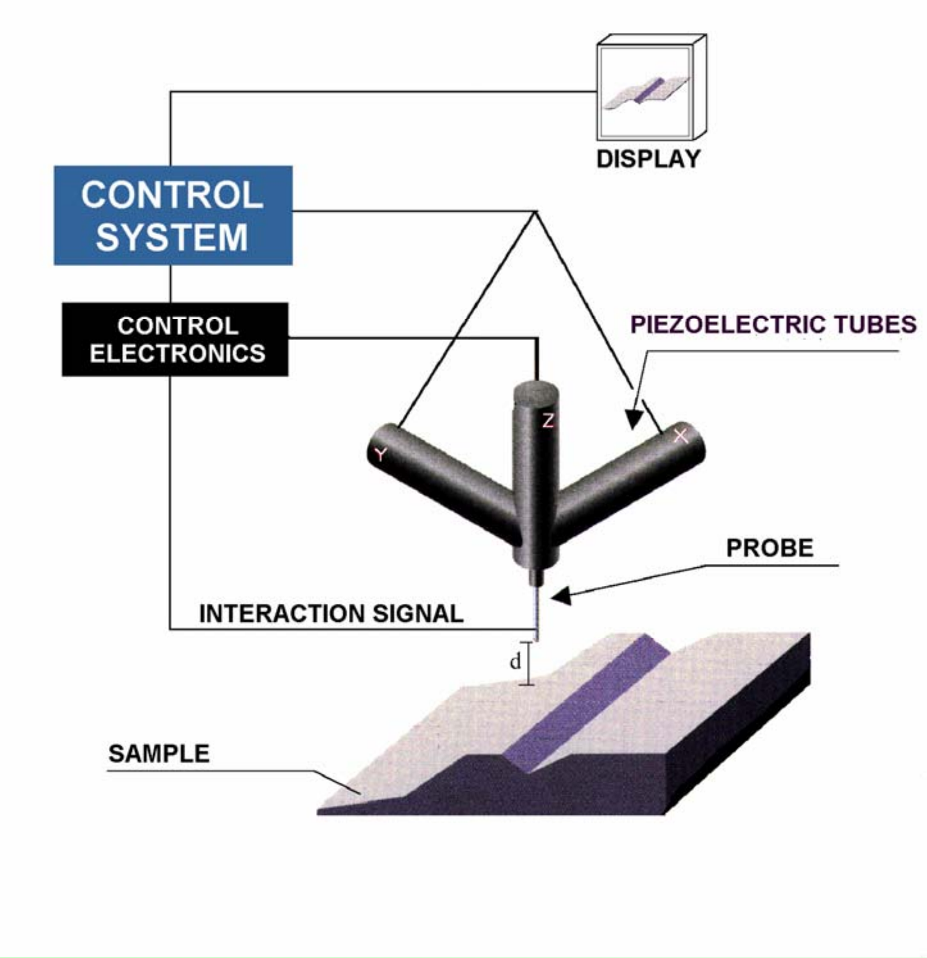


Fig. 1. Schematic illustrations of (a) experiment, (b) coated tips, (c) operation in liquid, and (d) semiconductor coated tip. See text for further details.

Scanning Tunnelling Microscopy

<u>Principe</u>: transfer of electrons from one conductor to another through an isolator.



Distance between electrodes: few Å

$I \cong$ nA

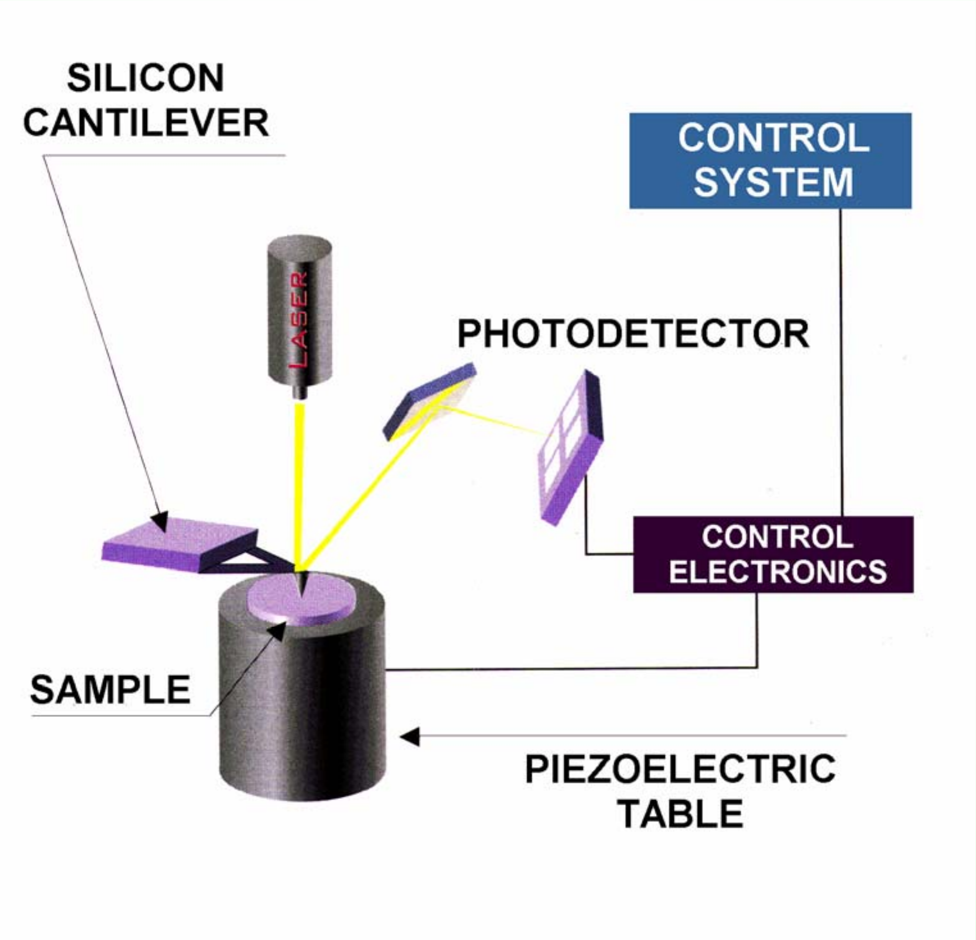
$I \propto \exp(-d)$: vertical resolution

Variations of I or d depend on the density of electronic states.

<u>Regulation</u>:
current I and position of the sample.

Atomic Force Microscopy

<u>Principe</u>: interaction between cantilever and surface.



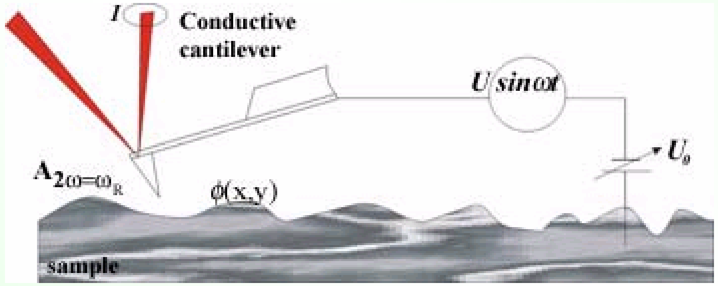
Allows to analyse both isolated and conducting surfaces
forces $\cong$ nN

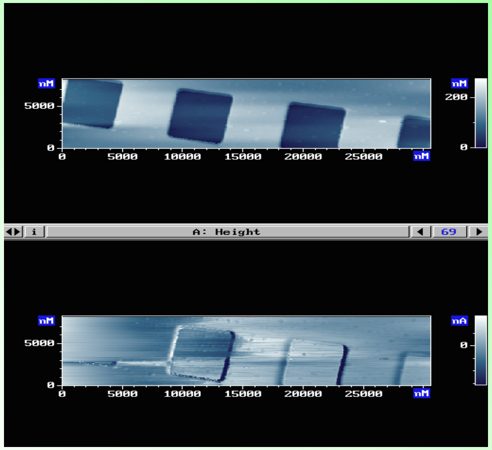
Displacements of cantilever gives:
- topographic information
- information on interaction forces between cantilever and surface

<u>Regulation</u>:
the value of the cantilever deflection and the position of the sample

An other possibility to collect electrons signal:

SCANNING CAPACITANCE MODE





Capacitor (Tip – Sample) energy:

$$E = \frac{CU^2}{2}$$

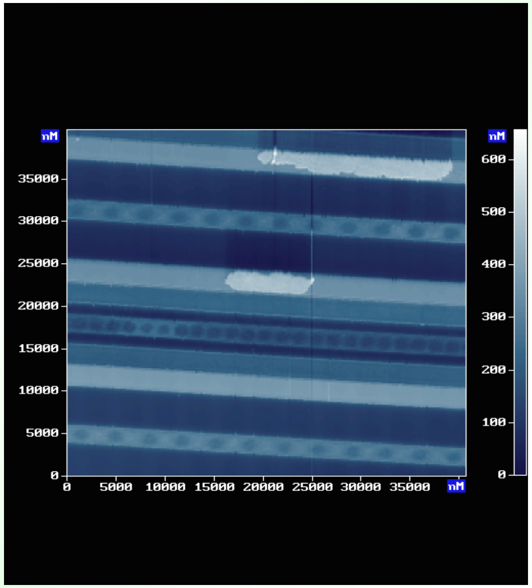
Attractive force:

$$F = \frac{\partial E}{\partial Z} = -\frac{1}{2} U^2 \frac{\partial C}{\partial Z}$$

If $U = U_0 + U_1 \sin \omega t$

$F1 = - U_0 * U_1 \sin \omega t$ **(1st harmonic signal)**

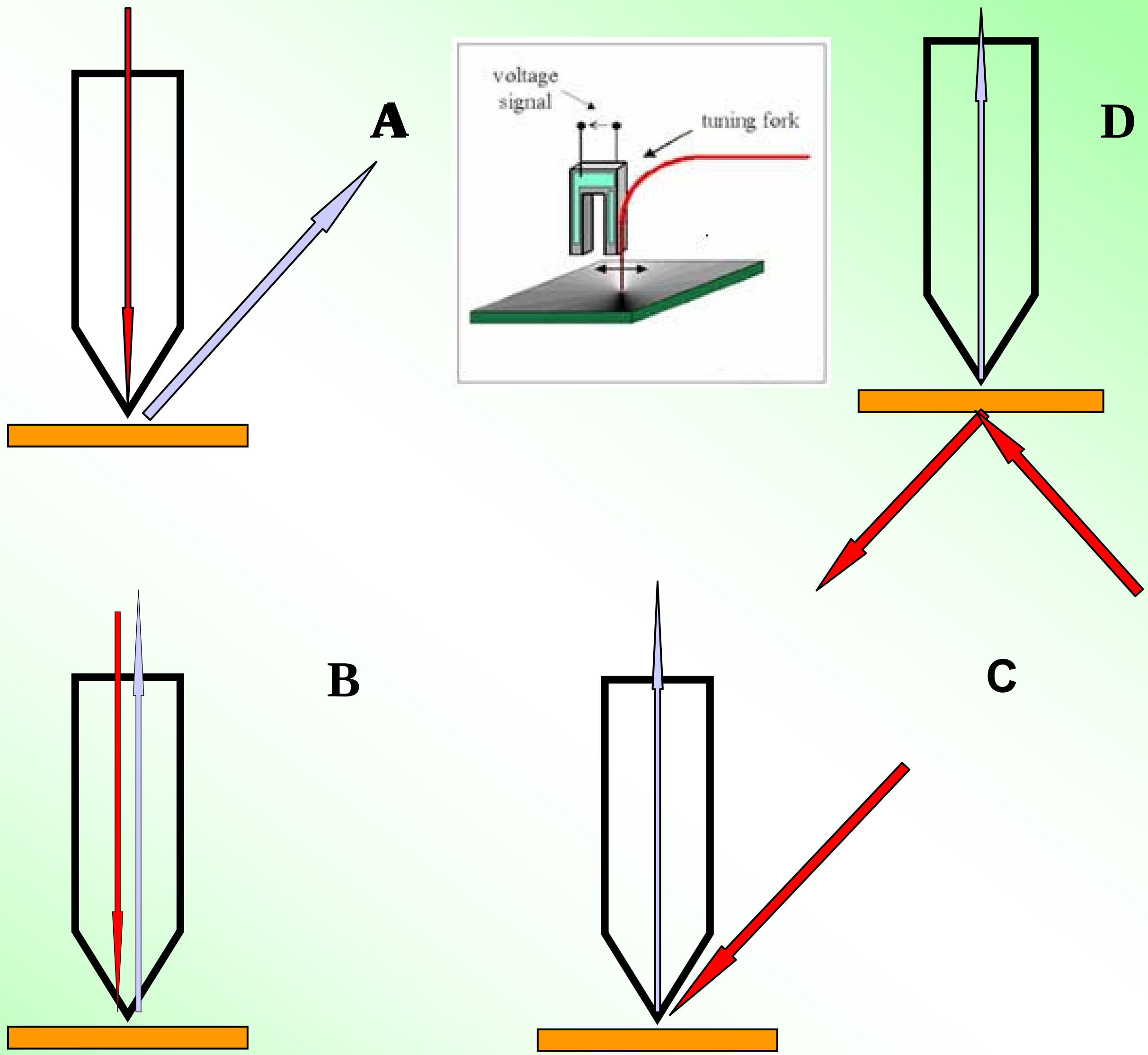
$F2 = 1/2\ U_1^2 \cos 2\omega t$ **(2nd harmonic signal)**



More informations:
http://www.ntmdt.ru/SPM-Techniques/SFM/Many-pass_techniques/Scanning_Capacitance_Microscopy_mode48.html

SNOM MODES

A: Excitation NF
Signal FF
B: Excitation NF
Signal NF
C: Excitation FF
Signal NF
D: Excitation FF
Signal NF



Element-Specific Contrast via X-ray absorption STM (XASTM) and Nano-XAS

- *Element-Specific Contrast in Scanning Tunneling Microscopy via X-ray absorption STM (XASTM).* Through appropriate selection of two energies - one before the element K- (or L-, M-) absorption edge and the second above the selected absorption edge of element, an *element-specific contrast* will be obtained substracting the photoemission and/or tunneling currents (before and above the edge) using the *local probe of STM*.

Nano-XAS: far- and local-probe

- **STXM** **Scanning Transmission X-ray Microscopy (far-probe)**
- **PEEM-XAS** **PhotoEmission Electron Microscopy (far-probe)**

  secondary electrons detection by electron microscope (in vacuum)
- **SNOM-XAS** **(local-probe)**

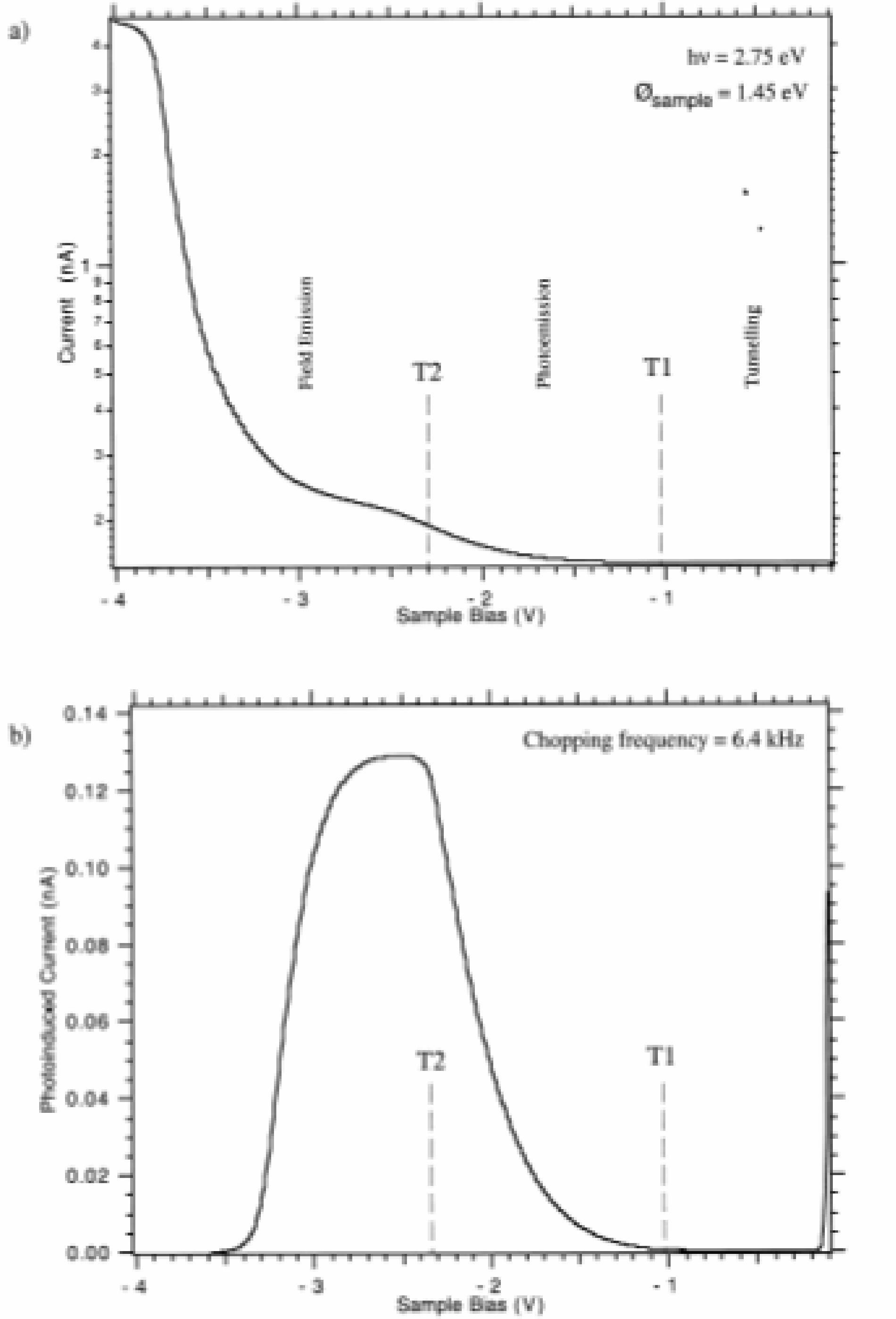
  x-ray excited optical luminescence (XEOL) detection by SNOM (in air & vacuum)

- **STM-XAS** **(local-probe)**

  a)secondary electrons detection in STM-mode by conductive tip
  (in vacuum)

  b) secondary electrons detection by AFM conductive tip (in vacuum)
- **CSM-XAS** **(local-probe)**

  detection by AFM conductive tip changes in the capacitance
  (in air & vacuum)



S.M. Gray
Photoemission with the STM
J. Electron Spectroscopy
J. Electron Spectrosc. Relat. Phenom. 109 (2000) 183-196

Fig. 7. (a) An *I–V* taken on the Cs/Al(111) surface with the feedback loop off and with the tunnel junction illuminated with chopped 458 nm (2.75 eV) light. The thresholds T1 and T2 separate regions where the current is dominated by tunnelling, photoemission and field emission. The roll-off in current below 23.8 V is due to saturation of the current amplifier. (b) The photo-induced current, measured simultaneously with (a) using lock-in detection at the laser chopping frequency.

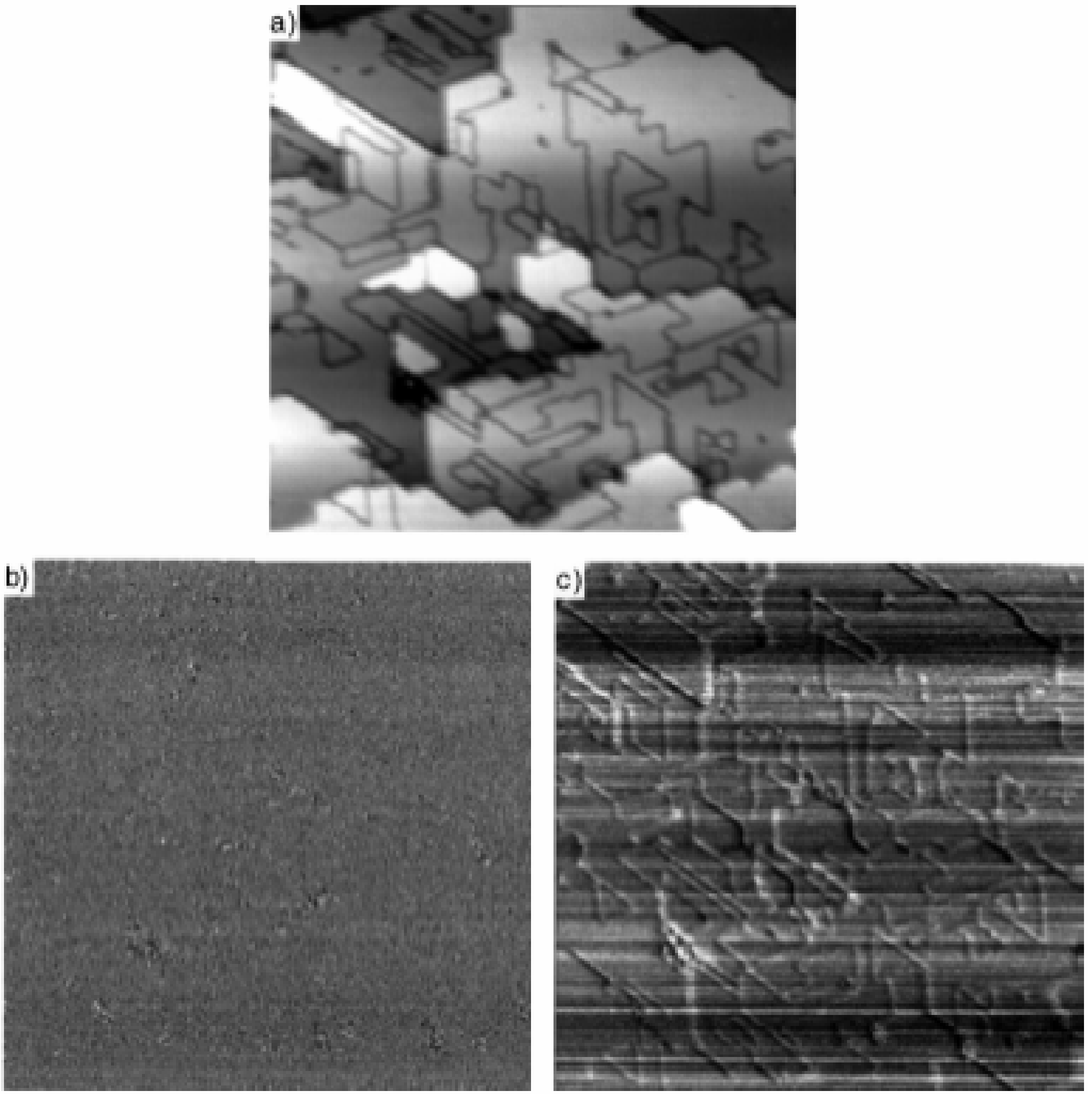
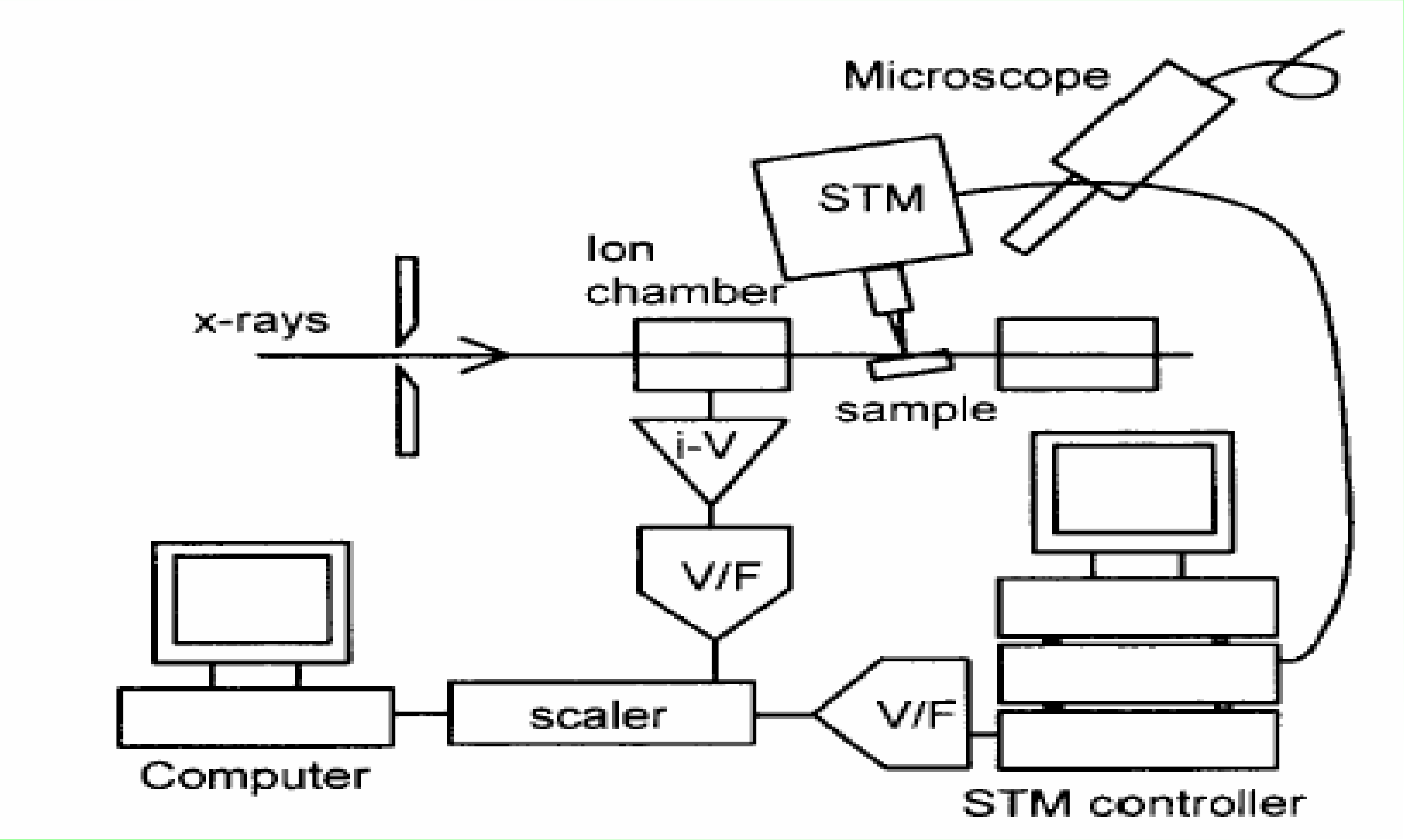


Fig. 5. (a) A topograph of the Rb/Al surface showing an area with many domain boundaries (1000×1000 Å, $I_t = 1.5$ nA). (b) A simultaneously acquired photocurrent map taken on the forward scan at a tip bias of 1.55 V. (c) The photocurrent map taken on the backward scan at a tip bias of 1.65 V. The first map's voltage is 0.05 eV below the threshold for detection of photoelectrons and the second 0.05 eV above it.

Experimental set-up on an STM under Sinchrotron Radiation



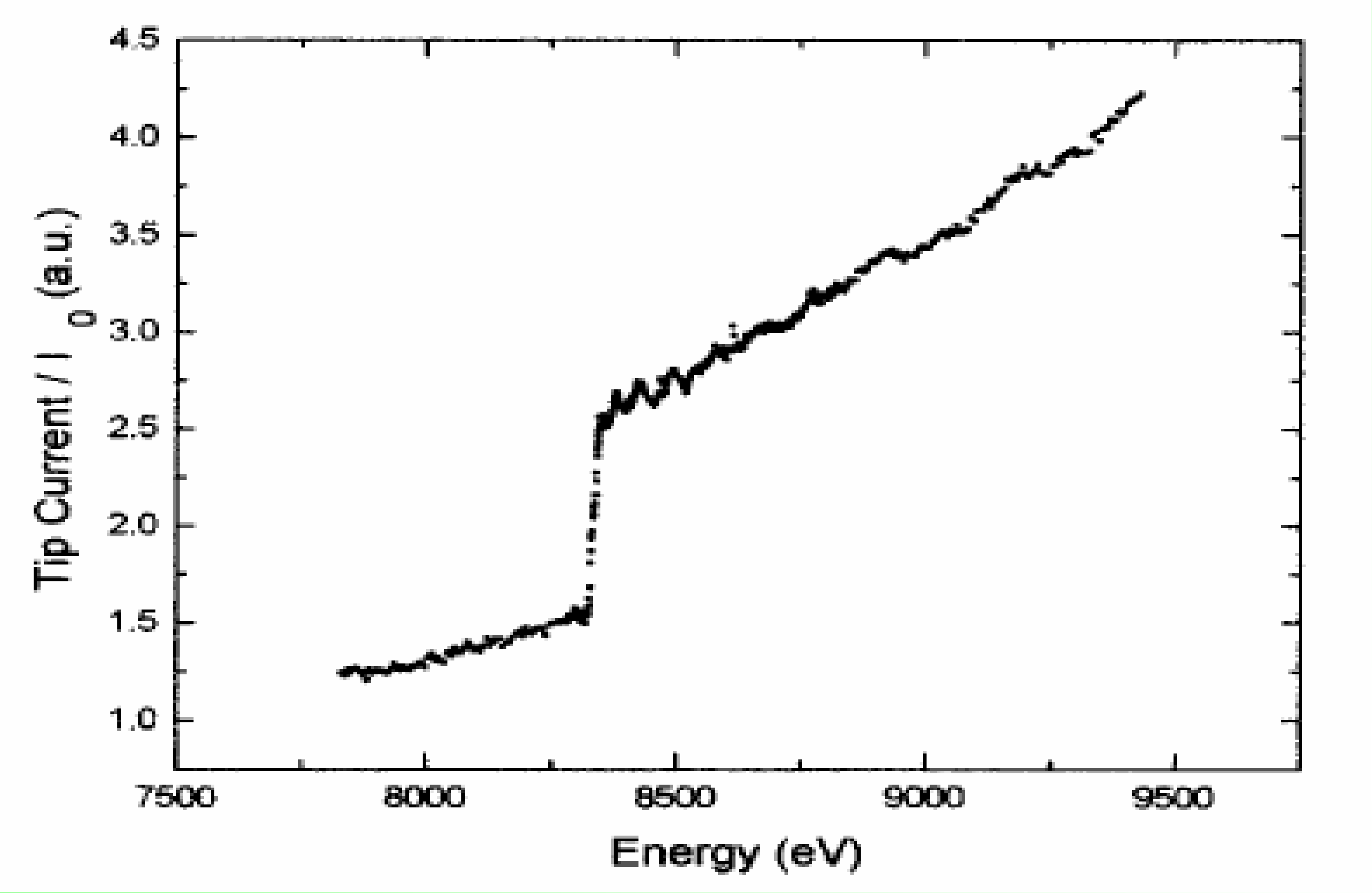
K.Tsuji Surf. Interface Anal. 27 (1999) 132

SURFACE AND INTERFACE ANALYSIS

Surf. Interface Anal. 27, 132-135 (1999)

EXAFS- and XANES-like Spectra Obtained by X-ray-excited Scanning Tunneling Microscope Tip Current Measurement

Kouichi Tsuji et al. **...** Japan



REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 75, NUMBER 6 JUNE 2004

Development and trial measurement of synchrotron-radiation-light-illuminated scanning tunneling microscope

Takeshi Matsushima, Taichi Okuda, Toyoaki Eguchi, Masanori Ono, Ayumi Harasawa, Takanori Wakita,[a] Akira Kataoka, Masayuki Hamada, Atsushi Kamoshida, Yukio Hasegawa, and Toyohiko Kinoshita[b]
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(Received 25 November 2003; accepted 2 February 2004; published online 24 May 2004)

Scanning tunneling microscope (STM) study is performed under synchrotron-radiation-light illumination. The equipment is designed so as to achieve atomic resolution even under rather noisy conditions in the synchrotron radiation facility. By measuring photoexcited electron current by the STM tip together with the conventional STM tunneling current, Si $2p$ soft-x-ray absorption spectra are successfully obtained from a small area of Si(111) surface. The results are a first step toward realizing a new element-specific microscope.
[DOI: 10.1063/1.1710708]

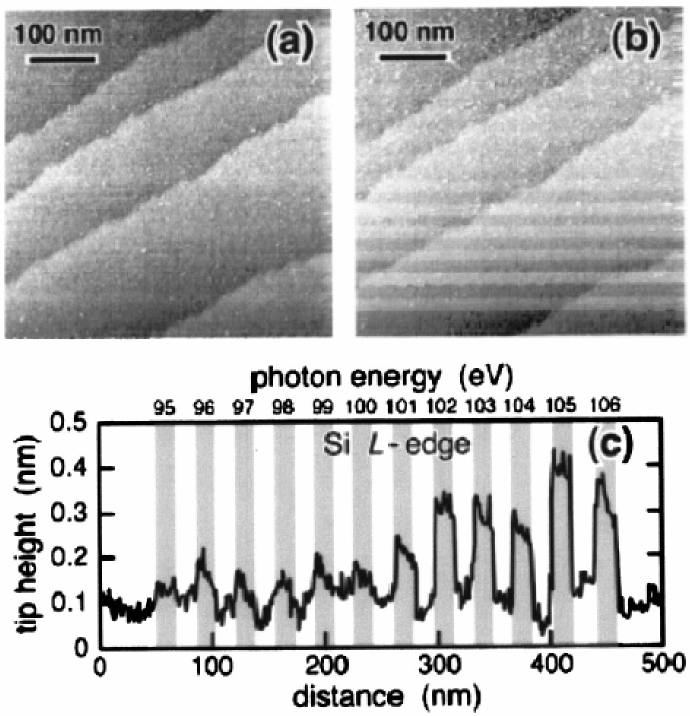


FIG. 6. (a) The STM image of the Si(111) surface. The image was measured with constant-current mode. The field of view is 500 nm × 500 nm, sample bias is −2.0 V, and tunneling current is set at −2.0 nA. (b) Same as in (a) but under the SR irradiation. The photon energy is scanned around the Si *L* edge threshold. (c) The shift of the tip height during the measurement in (b). The hatched areas correspond to the duration of the illumination, and the others are for not-illuminated (the beamline shutter was closed).

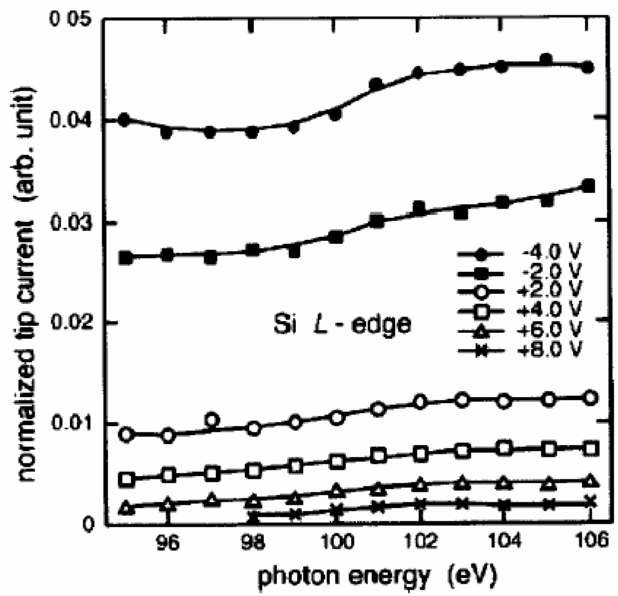


FIG. 7. The results of the tip current measurements as a function of the incident photon energy. The intensity is normalized by the incident photon flux measured by the mesh beam monitor placed at the upstream of the beamline. The bias condition for each curve is shown in the inset. The typical tip current is about 550–750 pA for −4 V bias and about 10–30 pA for +8 V.

sured. This procedure had been performed for various photon energies at several-bias voltages. As a result, when the sample was biased with the negative voltage (−2 and

Experimental set-up on an SCM under Sinchrotron Radiation , M.Ishii *NIM 1999 (2003) 205*

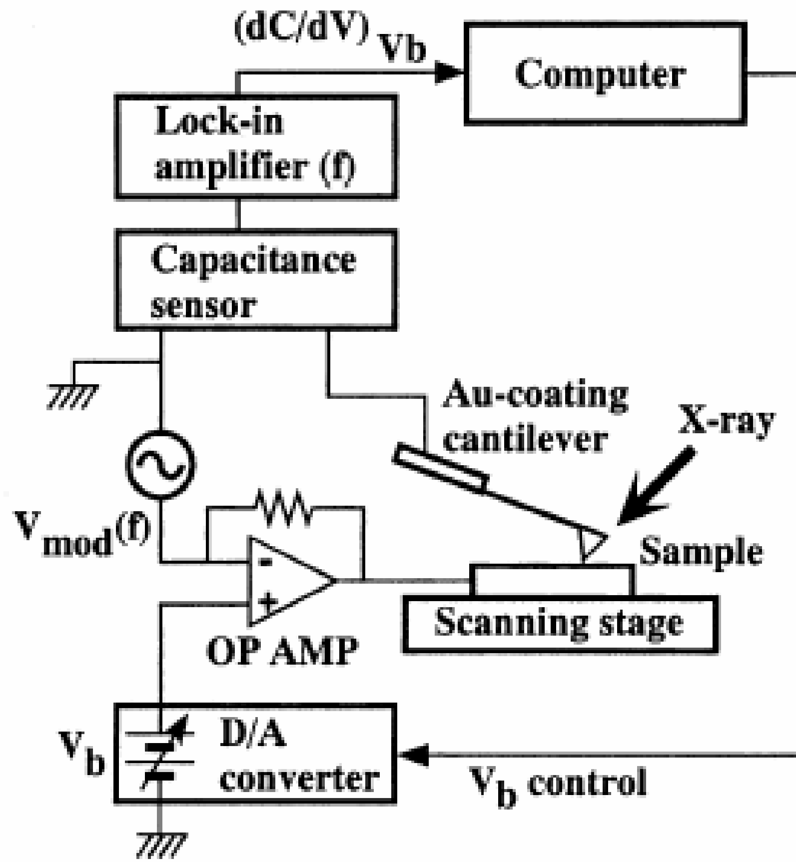
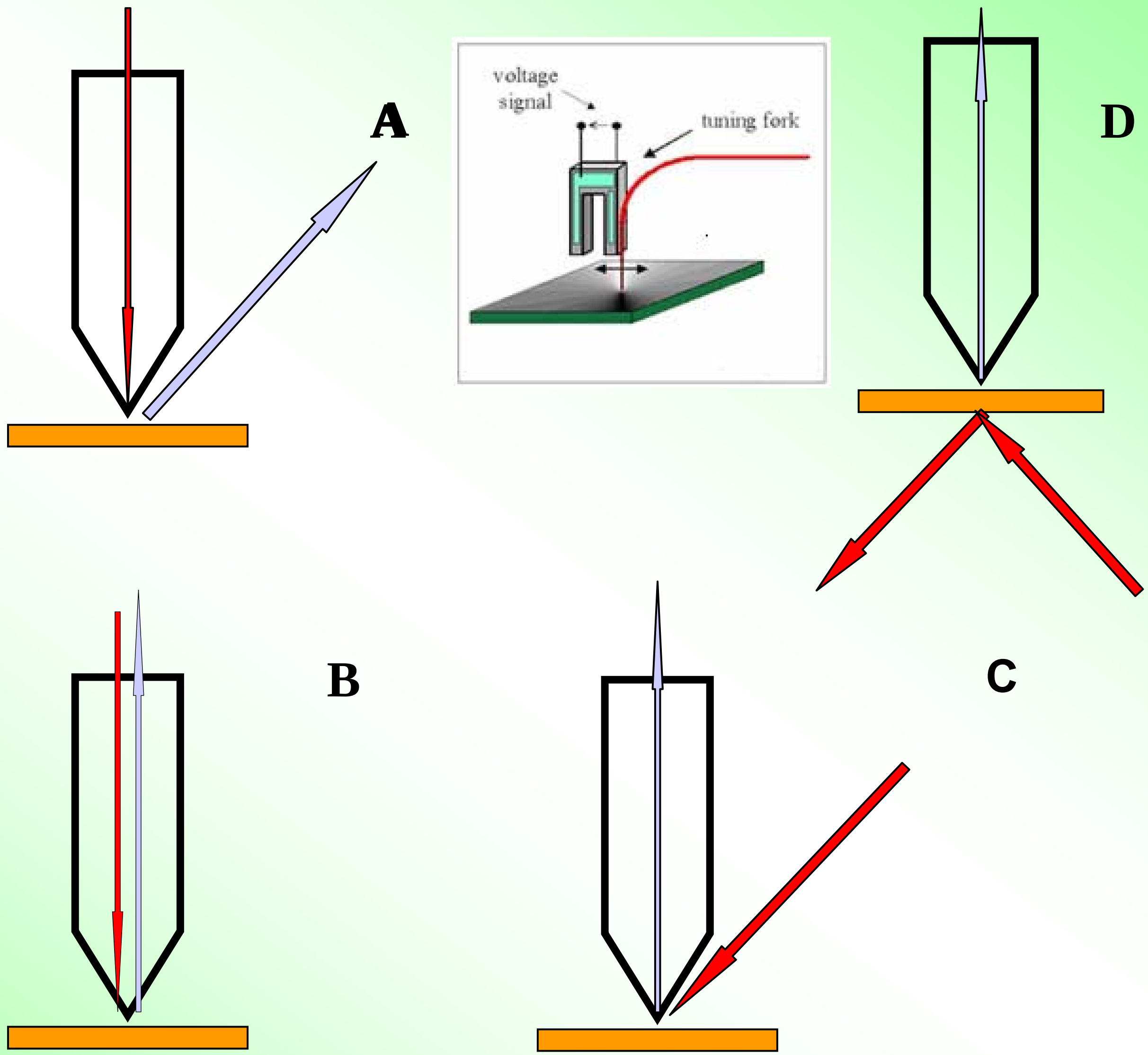


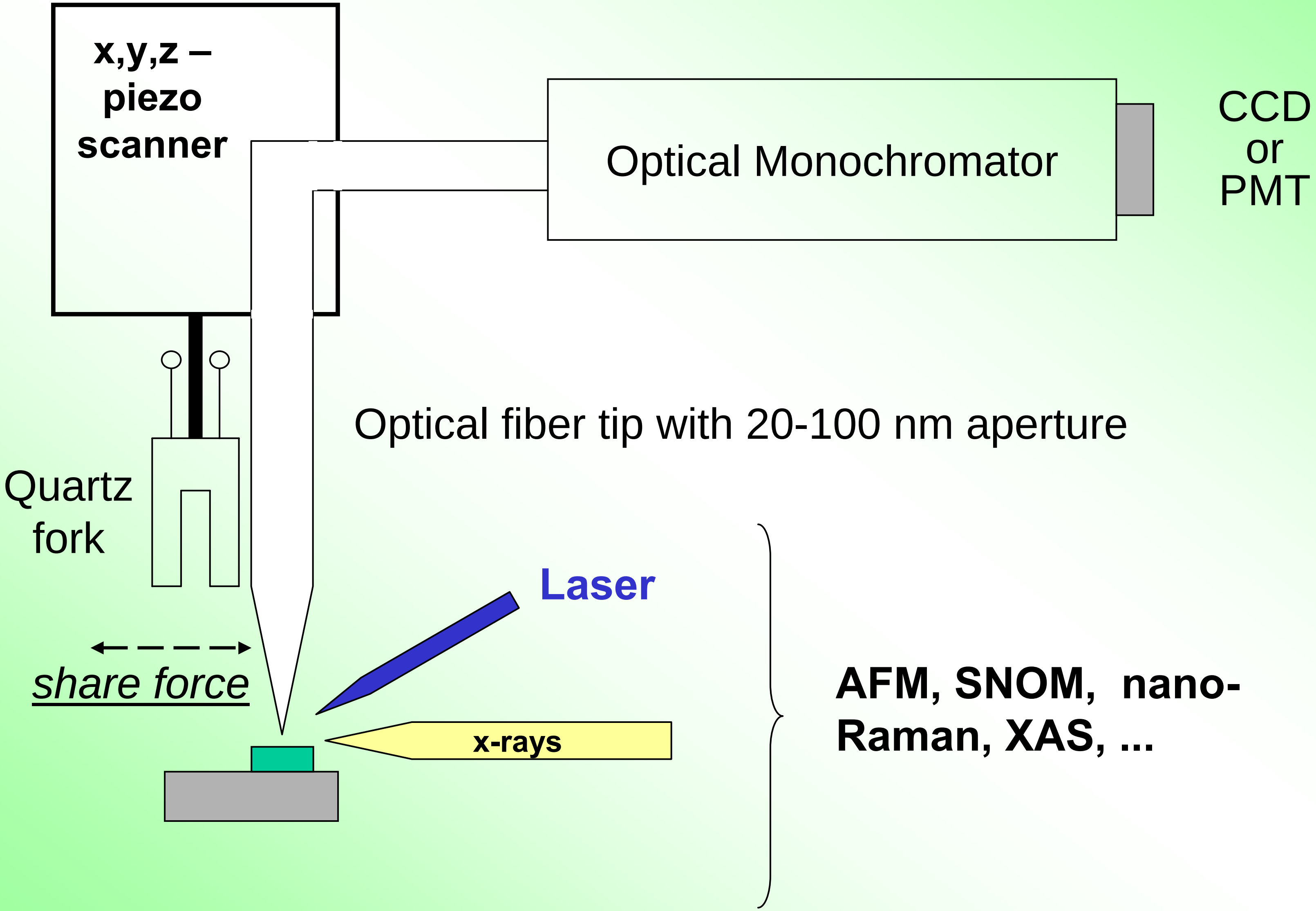
Fig. 2. Schematic diagram of the experimental apparatus for DORCAS developed in this study.

SNOM MODES

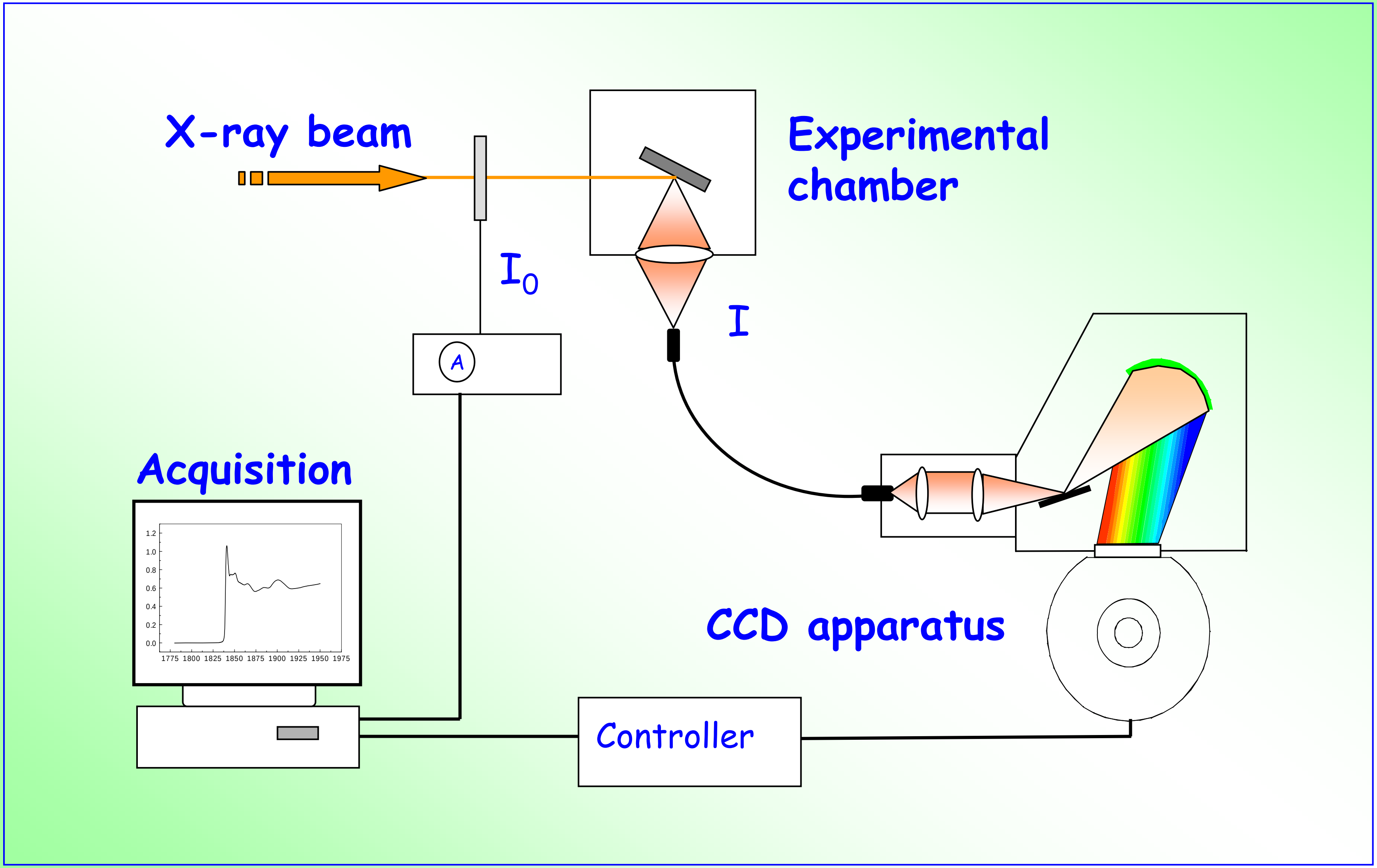
A: Excitation NF
Signal FF
B: Excitation NF
Signal NF
C: Excitation FF
Signal NF
D: Excitation FF
Signal NF



SNOM + X-RAY + Laser



PLY apparatus

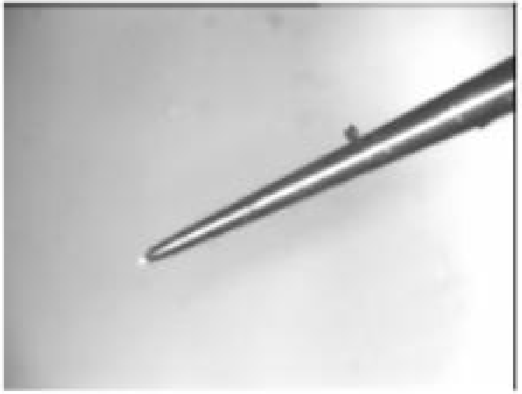


CRMC-N

X-TIP, One year

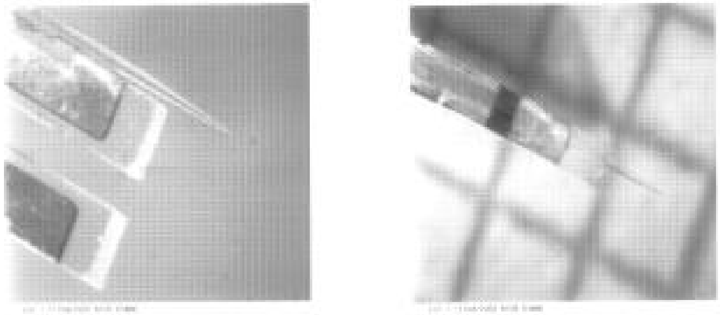
Tips improvement

Pulling
(Marseilles)



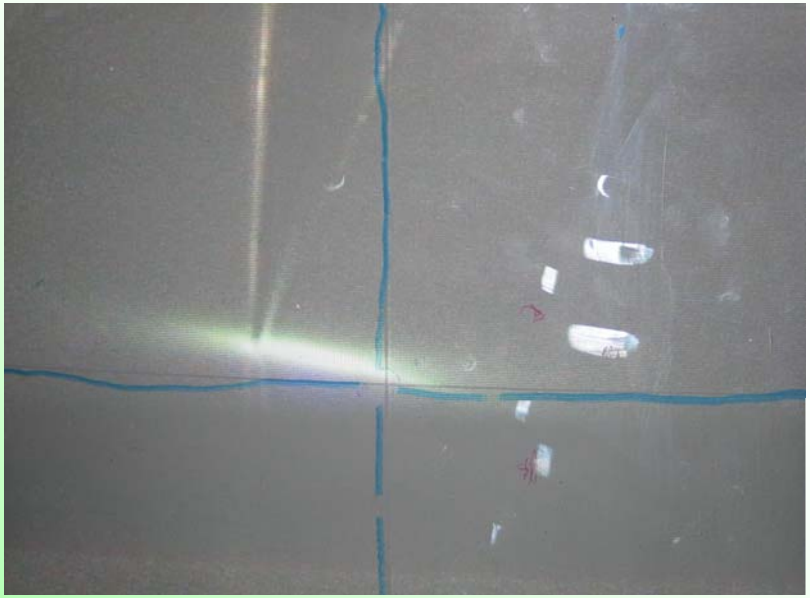
Coating

(Trento)

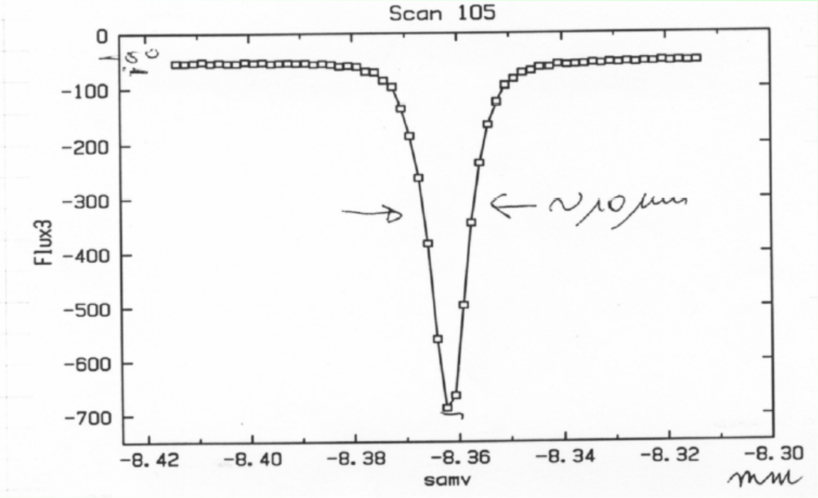


Sticking
(0.5 mm out of fork's prong)

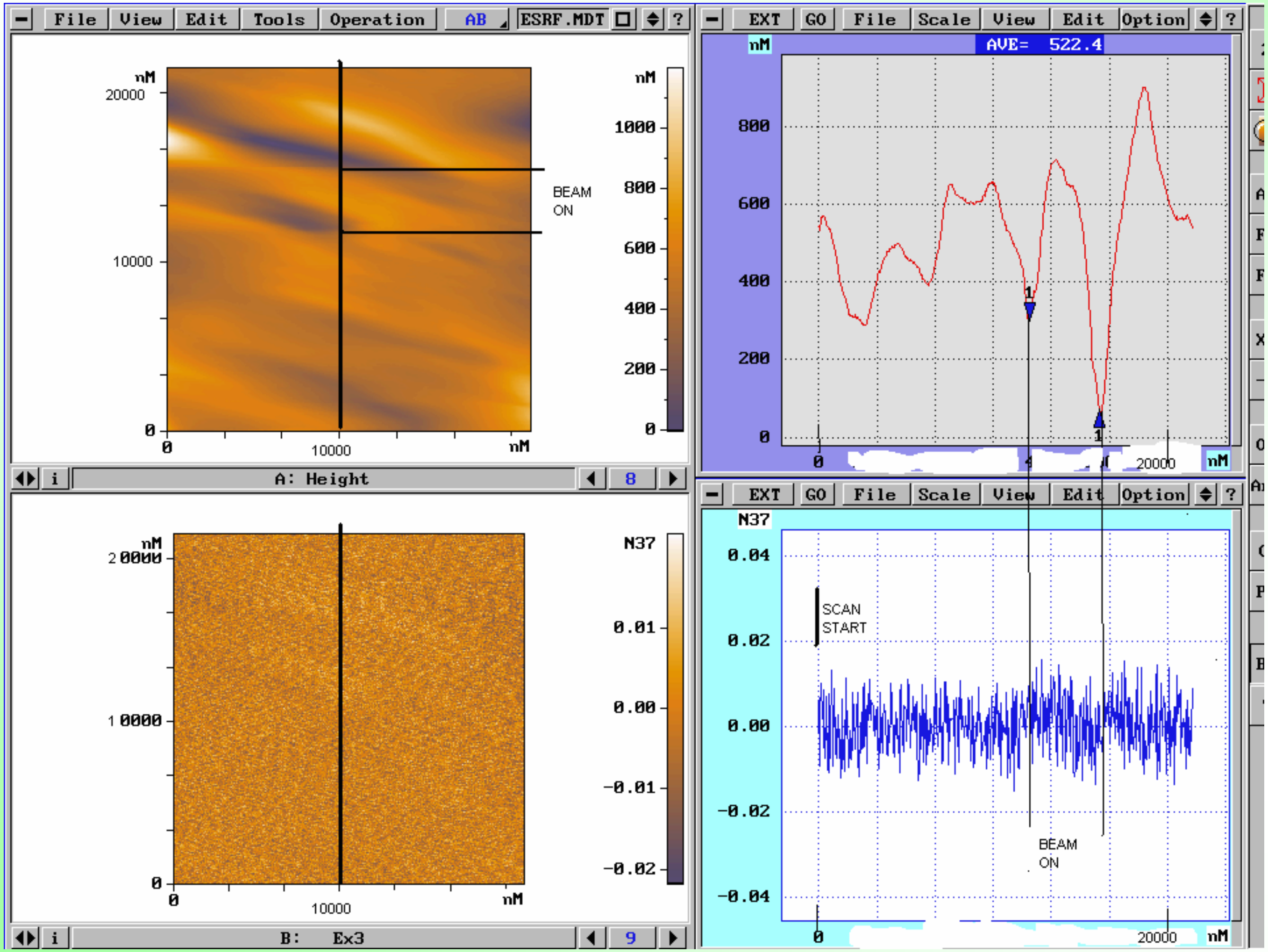
TIP-SAMPLE-BEAM ALIGNMENT



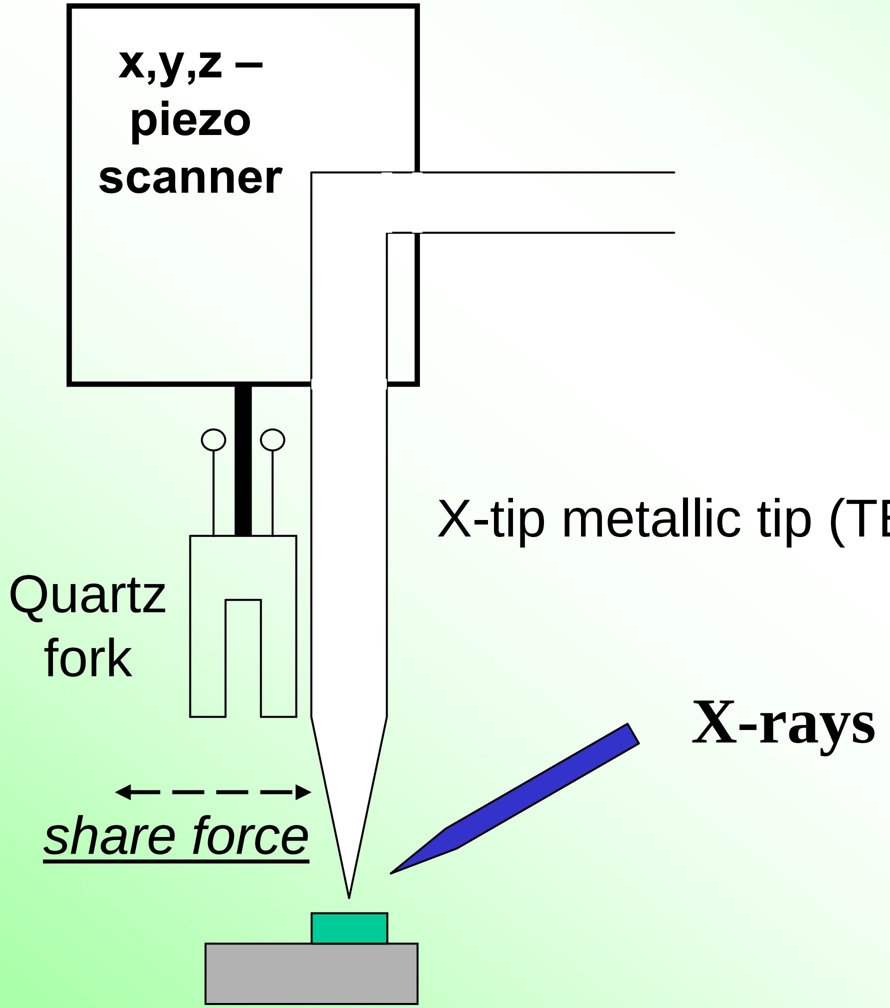
Lateral scan:
light intensity (SNOM)



X-TIP SNOM: imaging is possible and it is possible to collect light

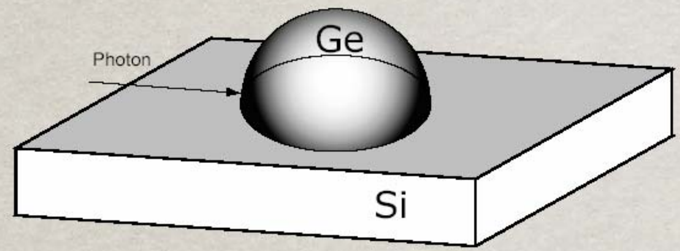


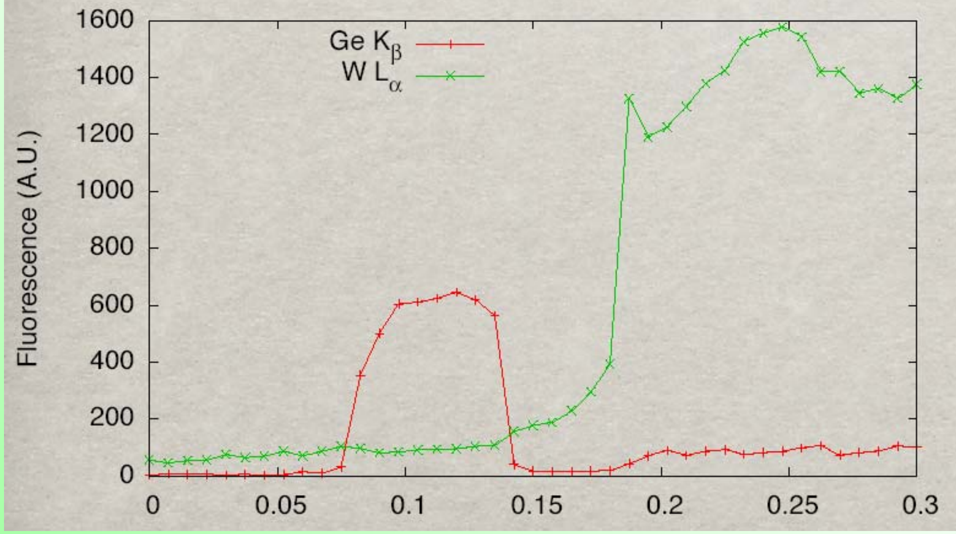
X-TIP Microscope principle



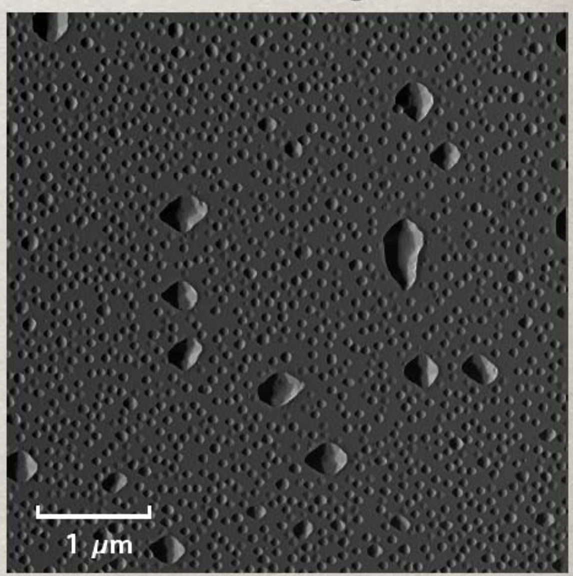
Sample

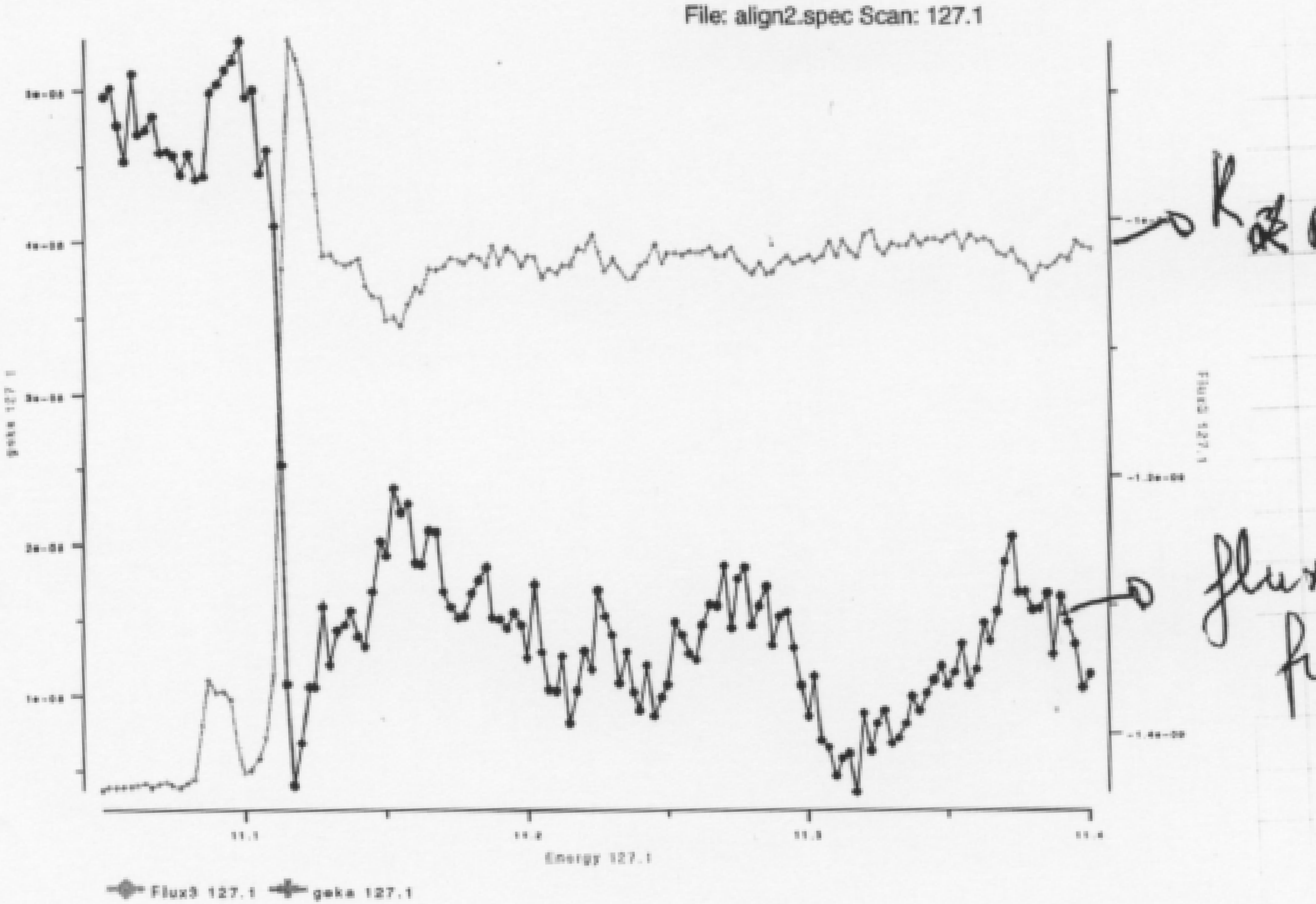
Ge dots on Si

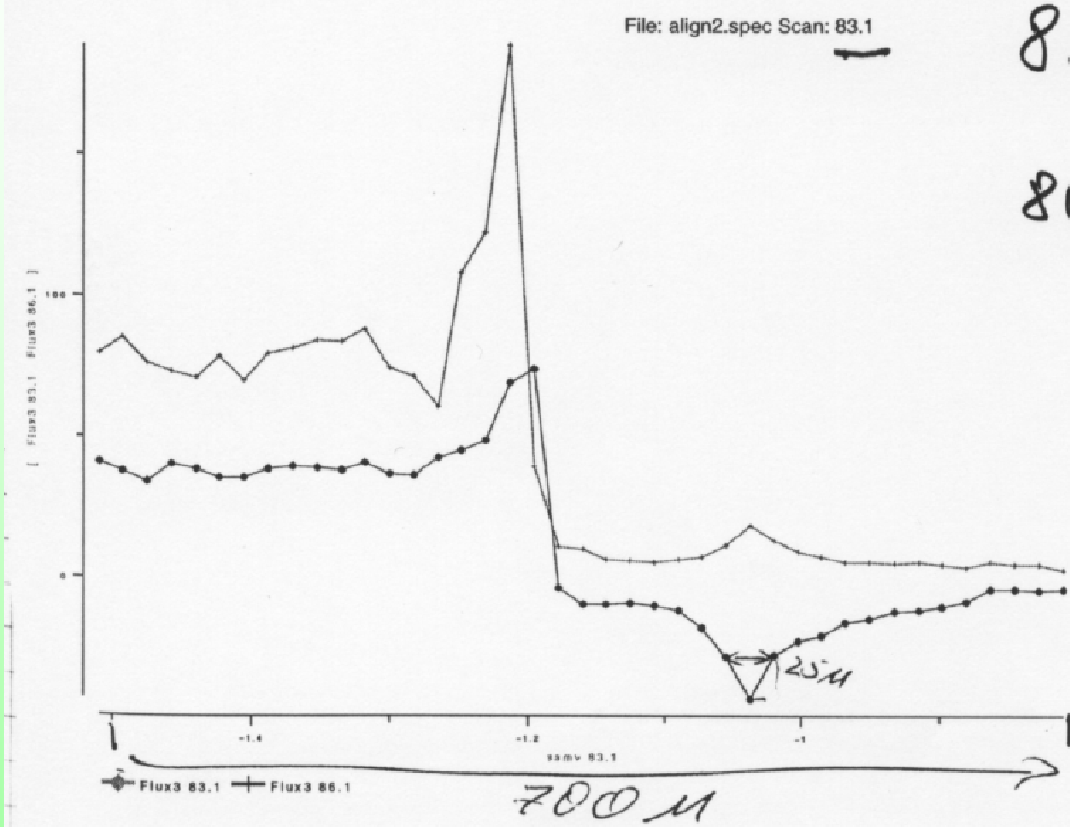




AFM Image




File: align2.spec Scan: 127.1
geka 127.1
Flux3 127.1
Energy 127.1
Flux3 127.1 geka 127.1



83 pol. + V.(Tip)

86 pol — V(tip)

ΔZ —

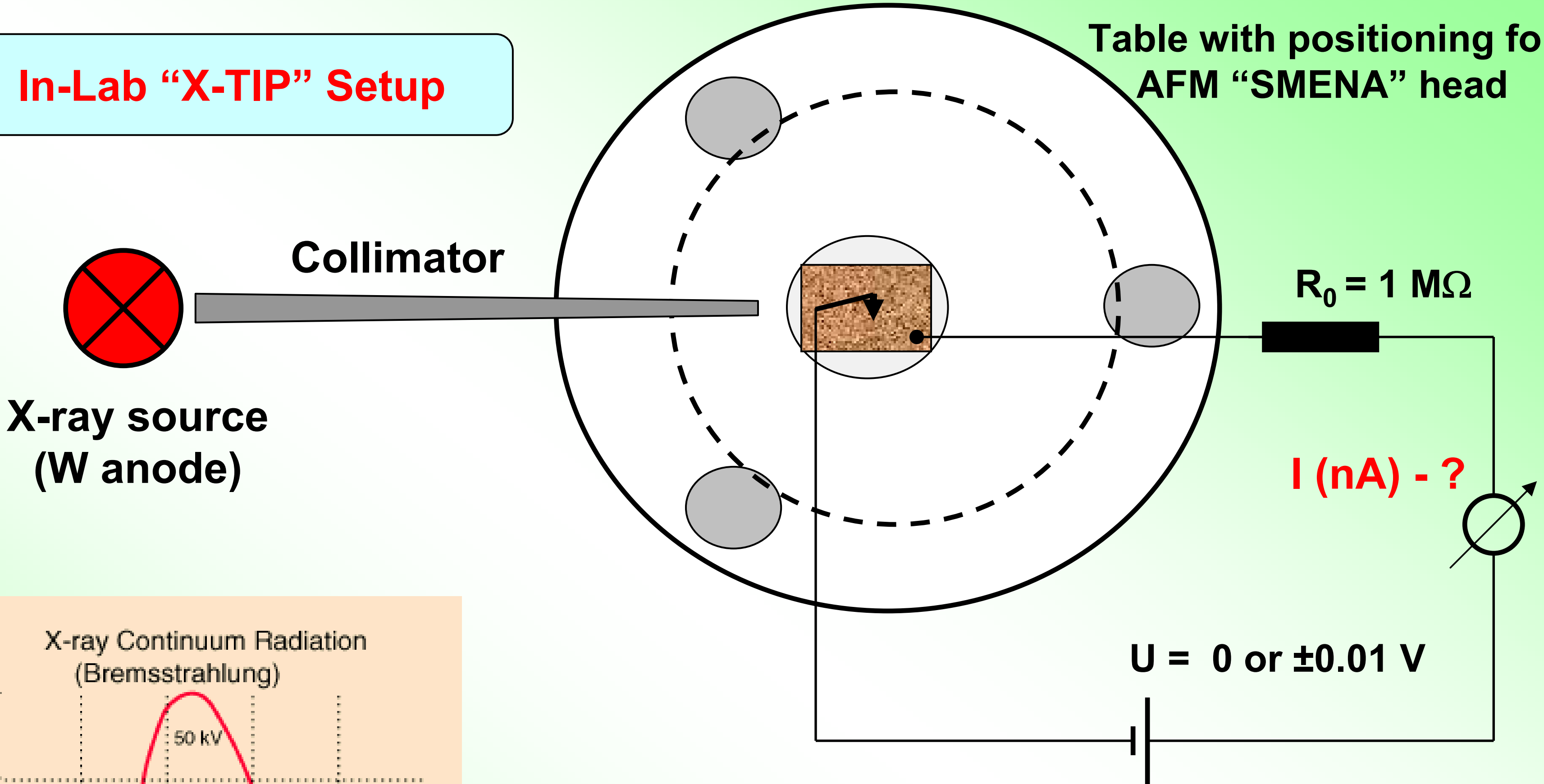
Development of LAB-XTIP

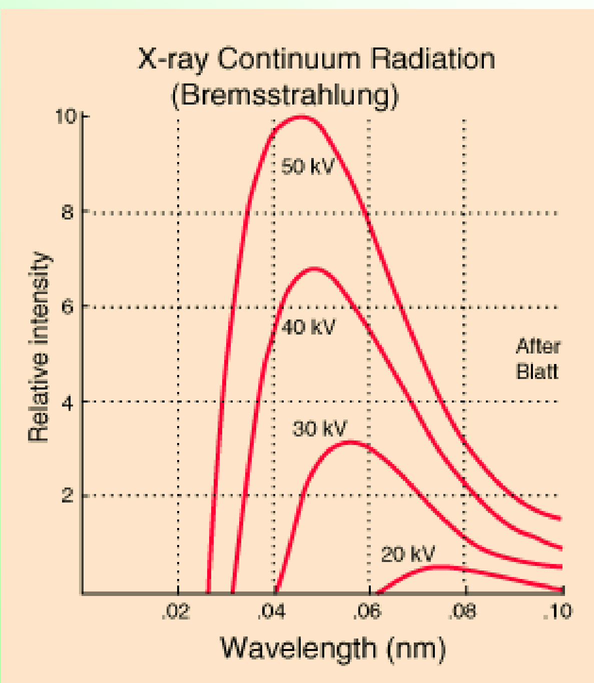
The development of LAB-XTIP new instrumentation is feasible due to the enormous progresses in the focusing X-Ray Radiation in-lab sources that ensure detection of required experimental signal from strongly confined, nano-scaled regions.

Two different ways will be explored :

- a cantilever (with the measurement hole of 50-100 nm) as a *collimator* of the focused X-ray beam on the cantilever;
- a cantilever as a *local probe detector* of the emission signals due to X-Ray processes in the sample.

In-Lab “X-TIP” Setup



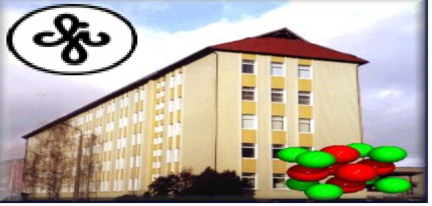


Change of X-ray conductivity

$$\Delta\sigma = e\,\mu\,\Delta n = e\mu\,\alpha\,\beta\,I_x\,\tau$$

where

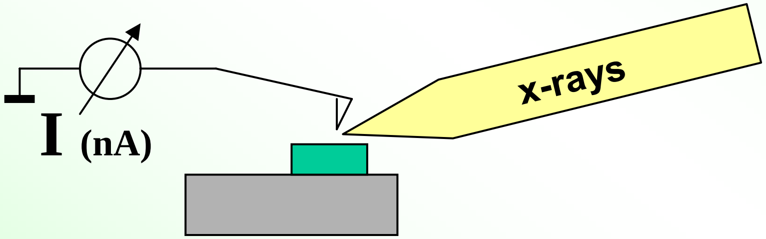
- e – electron charge,
- μ – mobility of charge carriers,
- Δn – change of charge carriers concentration,
- α – linear x-ray absorption coefficient,
- β – quantum yield,
- I_x – x-ray intensity,
- τ – instant life time of charge carriers.



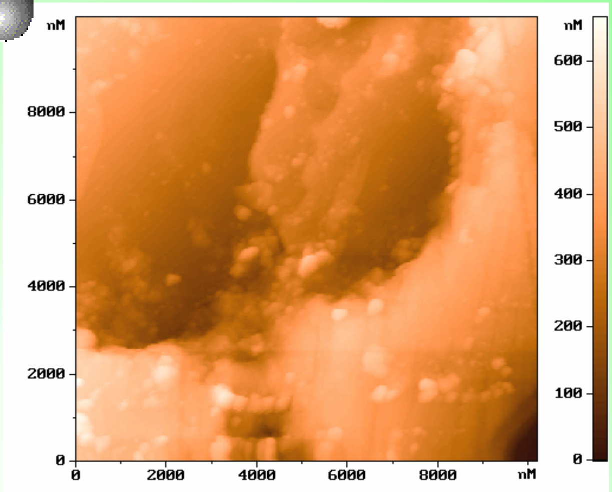
Riga, June 2001

GPEC

AFM + X-RAY EXPERIMENT



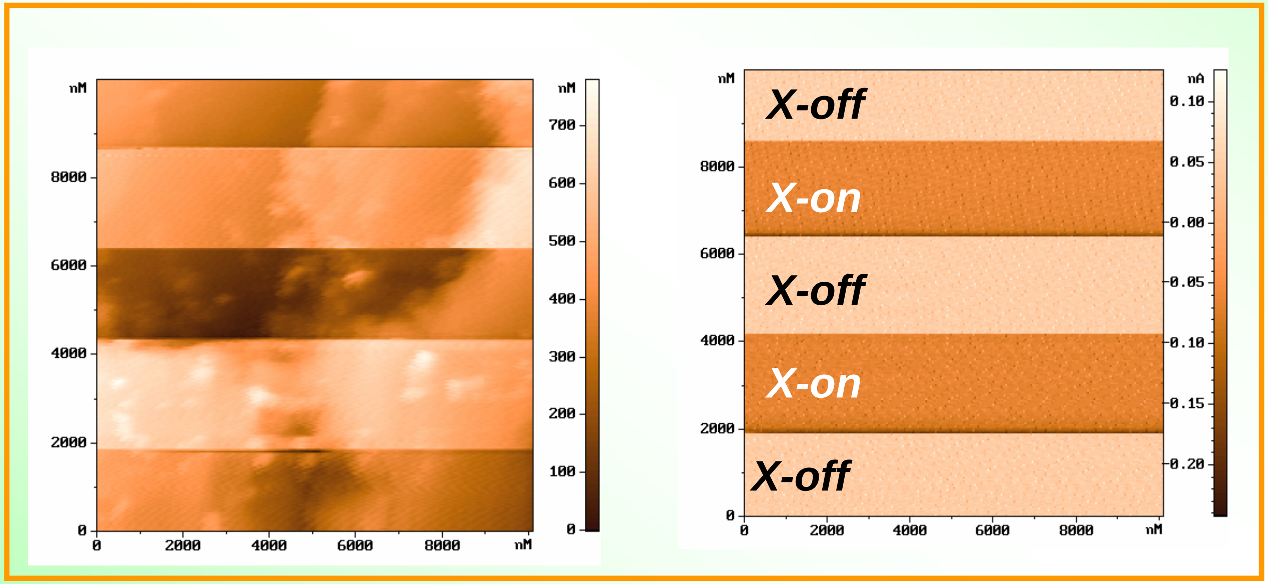
AFM topography scan



AFM + X-ray scan

Topography

Current



CONCLUSIONS

The preliminary results together with some basic considerations provide a platform for proposing that STM, AFM, SCM *can serve as useful local probe for X-ray « products» :*

•XAS-SNOM *– Element-Specific Contrast in Local Probe Microscopy via X-ray excited optical luminescence (XEOL) detection by optical probe in SNOM mode.*.

•. XAS-STM *– Element-Specific Contrast in Local Probe Microscopy via X-ray excited photoelectrons detection by conductive tip in STM mode.*

• XAS-AFM *– Element-Specific Contrast in Local Probe Microscopy via X-ray induced changes in capacitance by conductive tip in AFM mode*.