SNOM detection of X-ray excited optical luminescence using Synchrotron Radiation : A new tool for nanoscience

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Introduction

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)
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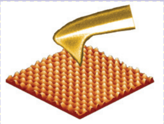
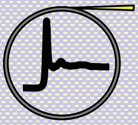
Scanning Probe Microscopies (SPM) have already made a huge impact in nanoscale materials science as surface sensitive techniques. Unfortunately they are not element specific and they are sensitive mostly to the surface morphology. This is a shortcoming since many materials are inhomogeneous over local element composition.

X-ray absorption spectroscopy (XAS) techniques probe the electronic and structural properties of materials. Their main limitation is the lack of lateral and vertical resolution. This is a problem since many materials properties are inhomogeneous over a much smaller scale.

Idea



Scanning Near-Field Optical Microscopy (SNOM)



X-ray Excited Optical Luminescence (XEOL)

Element-Specific Contrast in SNOM and Local X-ray Absorption via near-field XEOL detection

XAS-SNOM microscope head

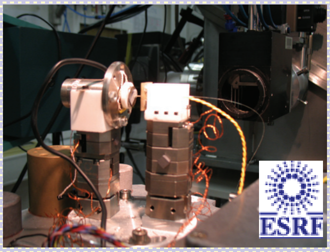
SNOM aperture configuration in collection mode: an optical fiber tip with a sub-wavelength aperture acts as detector of the x-ray excited optical luminescence emitted by the sample.

Shear-force tip feedback for the tip-sample distance regulation and for recording the topographic image.

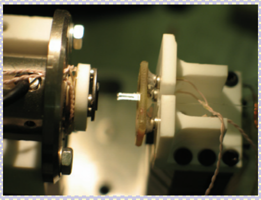
6 independent-axis nanopositioning system to align sample and tip with respect to the x-ray beam; **scan of the sample under tip** to keep the tip fixed during the scanning.

Two highly sensitive detectors connected to a spectrograph/monochromator.

Integration of the X-TIP instrumentation with the beamline software control and data acquisition system to guarantee the synchronized and automatic management of the measurement process.



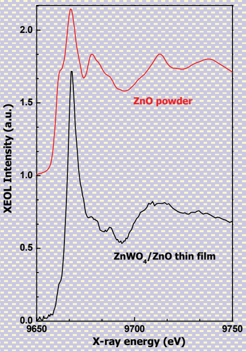
XAS-SNOM microscope head at ID03 beamline.



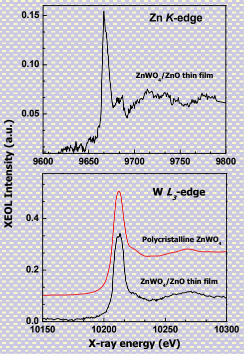
Sample and tuning fork holder

Experimental results

Far-field

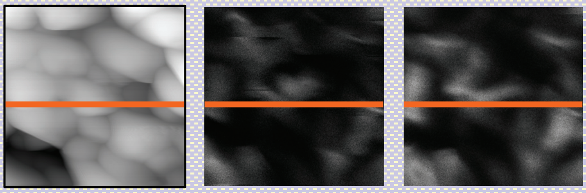


Near-field

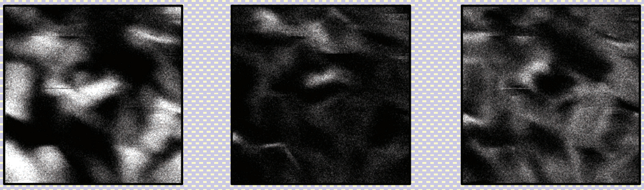


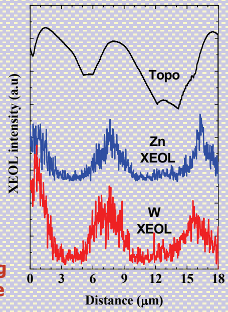
XEOL-XAS of Nanostructured thin films

Topography | **XEOL Contrast at the Zn *K*-edge** | **XEOL Contrast at the W L_3-edge**



XEOL signal increasing at both edges | **XEOL signal increasing *only* at the Zn *K*-edge** | **XEOL signal increasing *only* at the W L_3-edge**





Topographic image and different XEOL-contrast images obtained at the Zn *K*-edge and at the W *L3*-edge in mixed $ZnWO_4$/ZnO thin films.
The images size is 18x18 micron.

Conclusions

We have developed a modular and sturdy XAS-SNOM microscope head, conceived to work in conjunction with x-ray microbeams.

The prototype has been installed at ESRF BM05 and ID03 and successfully integrated with the beamlines software control and data acquisition systems. Thanks to the energy tunability of synchrotron radiation, near-field XAS-XEOL spectra have been acquired using the optical fiber tip to probe single nanostructures. Moreover, the XAS-SNOM prototype has been used to perform simultaneous topographic and chemically sensitive optical imaging, at different absorption edges.

The new instrumentation has been employed to study luminescent nanostructured materials, in particular ZnO and ZnWO4 thin films.

The results indicate a non-homogeneous composition of the mixed $ZnWO_4$/ZnO fillm, which is composed of predominantly $ZnWO_4$ phase. However, zinc oxide is present in two phases - wurtzite-type and rock-salt. The latter phase, *r*-ZnO, normally existing at high pressure, is probably stabilized in the film due to the presence of the local stress present.

We would like to point out that the presence of ZnO phase is un-ambiguously detected only at nano-scale by XAS-SNOM method, that emphasizes the difference between the average macroscopic and local nanoscale structures.

References

S.Larcheri, F.Rocca, F.Jandard, D.Pailharey, R.Graziola, A.Kuzmin, and J.Purans, *Rev. Sci. Instrum*, **79**, 013702, 2008

S.Larcheri, F.Rocca, D.Pailharey, F.Jandard, R.Graziola, A.Kuzmin, R.Kalendarev, and J.Purans, *Micron* (in print)

X-TIP website: http://www.cfi.lu/xtip/