ESRF	**Experiment title:** X-TIP: XANES and Optical characterization of ZnO nanostructures using local probe detection with x-ray microfocussed beam excitation.	**Experiment number**: MI829
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Report:

Aim of the experiment

This experiment is in the framework of the Specific Targeted Research Project "X-Tip" (NMP4-CT-2003-505634), supported by the European Commission under the 6th Framework Programme. The project aims to merge the ability of Synchrotron Radiation (SR) spectroscopies in providing elemental composition, chemical status and structural information with the lateral resolution of Local Probe Microscopies (LPM). In particular, the main goal of the experiment is to test the new head for photon detection by Scanning Near-Field Optical Microscopy (SNOM) developed by the group of CRS-CRMCN (Marseille). In this way, we can verify the feasibility of **(a)** SNOM imaging by collecting the X-ray Excited Optical Luminescence (XEOL) signal at a fixed X-ray energy, within a selected area of the sample; **(b)** X-ray Absorption Fine Structure (XAFS) measurements in near-field condition by detection of XEOL spectra (ref. 1) at different X-ray energies, using a SNOM optical fiber probe.

Experimental

Our SNOM prototype is based on a shear-force system for the tip-sample distance regulation. It is provided with two totally independent towers of actuators (Attocube) for the nano-positioning of tip and sample along the three axis. The XEOL signal is collected by the optical fiber tip and, after passing through a monochromator/spectrograph, reaches a photomultiplier tube (PMT) characterized by a nominal gain of $1 \cdot 10^7$. The SNOM tips we used are fabricated by LovaLite company (France). After the fabrication and the metallization with Al, the tips are glued to an auto excited tuning fork head and mounted onto the piezo-actuators. The nominal apex radius of the tip is around 50-100 nm.

The measured values of the X-ray beam intensity at 9600 eV and of its size on the sample are 10^8-10^9 ph/s and ~2x3 μm^2, respectively. A Kirkpatrick-Baez (KB) focusing system was used for the collimation of the beam. All the required electronics and controls were installed within the experimental hutch and controlled remotely. Some modifications of the standard acquisition software were performed in order to synchronise the detection of X-ray beam and of XEOL intensity during the XAFS scans. This preliminary work was done previously in collaboration with ESRF's technical staff.

The samples used to test the prototype are a $CdWO_4$ single crystal and two ZnO thin films: TEC2 fabricated by atmospheric chemical vapor deposition and 341HT deposited by magnetron sputtering. These samples were selected among others because they exhibited a good photoluminescence both under laser light and X-rays from conventional sources. However, they are not just testing samples; our hope is also to contribute to a better understanding of the origin of their luminescence, by correlating their optical properties with the stuctural environment around the light emitting centres (as in ref. 2).

Main results

First of all, we set up an alignment procedure to place the SNOM tip exactly under the X-ray beam. It consists in scanning the tip vertically across the beam at different transverse positions, trying to minimize the signal measured by a Si detector placed after the prototype. In conjunction with the very accurate sample positioning systems of the beamline BM05 and of our SNOM prototype, this procedure allows a remote, quick and precise alignment.

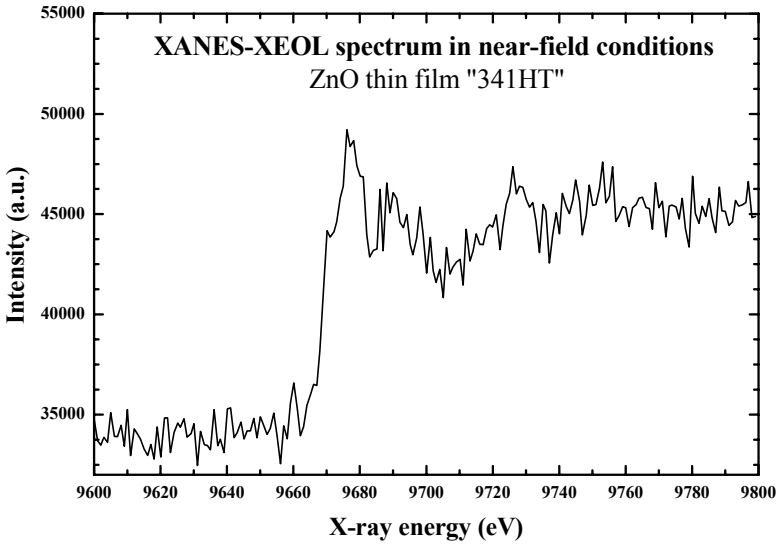
In the attempt to evaluate the effects of a long exposure of the SNOM tip to the SR light, we performed the imaging of our samples under X-ray irradiation and after closing the beam shutter. No difference or discontinuity in the

topographical image was observed. On the contrary, of course, the optical image registered a zero signal when the X-ray beam was switched off.

For the first time we succeeded in collecting the XEOL-XAFS spectra from all the samples in near-field condition. The figure below shows an example taken from the ZnO thin film "341HT", that is the sample with the lowest detectable photoluminescence (~$5 \cdot 10^3$ ph/s on the maximum of the optical luminescence band, excited at 9700 eV). The spectra acquired from the ZnO thin films present the absorption fine structures typical of ZnO and already investigated on the same samples in standard acquisition conditions at ESRF on BM08-GILDA. (ref. 2)

To complete our tests on the SNOM prototype and on the acquisition system, we performed also the optical imaging of our samples, that is, we collected the XEOL signal at a fixed X-ray energy while scanning the sample surface under the SNOM tip. The optical images acquired at different times on the same part of the sample surface and using the same experimental settings, showed a perfect reproducibility and a lateral resolution of a few hundreds nm.

Conclusions and future work



During this experiment we made a considerable breakthrough in showing that our SNOM prototype can operate in conjunction with focused X-ray SR beam. The hardware and the software of the instrument have been integrated in the beamline and an alignment procedure has been devised to correctly place the tip under the beam. The SNOM optical fiber probes fabricated by LovaLite seem to be good candidates for LPM applications in a SR facility since they don't undergo any damage after a long exposure to X-rays. However, the real dimension of the tip after a long use has still to be checked.

We demonstrated that it is possible to collect the XEOL signal emitted by a nanostructured sample by means of a SNOM optical fiber tip. The feasibility of such an experiment was not obvious at all since we are dealing with very weak signals. In fact, the intensity of the incident X-ray beam was quite low on BM05 and the XEOL signal itself is very weak since it comes from a small region of the surface (comparable in size to the tip aperture). To our knowledge, however, this is the first successful attempt (1) to measure in near-field conditions the XEOL-XANES spectrum using a SNOM tip to collect photons and (2) to acquire the near-field optical image of a nanostructured surface by detecting the optical luminescence emitted under X-ray synchrotron radiation.

In the near future, a lot of work has to be done to assess some issues and to solve the problems that still remain open.

We are devoting many efforts to improve the imaging resolution of the SNOM head. To reach our final goal of a lateral resolution below 100 nm, we can act at two different levels:

1. the stability of the beamline and of the instrument: it is extremely important to reduce the geometrical fluctuations of the beam on the sample and to compensate all the vibrations due to vacuum pumps, electronic devices, air conditioning systems,… present inside the experimental hutch. For example, the whole instrument could be equipped with a more effective antivibration system and protect using a glass bell against the air vibrations. In any case, we have also to deal with some beamline intrinsic vibrations and instabilities that are not eliminable.
2. the aperture size at the very apex of the tip: of course, the smaller the aperture, the higher the resolution. But the smaller the aperture, the higher the intensity of the X-ray beam needed to have a detectable XEOL signal. This means that, to improve the lateral resolution of our SNOM prototype, we need a SR beam much higher than the one we had on BM05. In the next future, we hope to have access to ID03 or ID22, where the SR source is an insertion device. We are also looking for less fragile SNOM tips, able to guarantee a good lateral resolution also after several scannings over the sample surface.

Another important issue is the search for samples well suited to test the prototype. Untill now we have investigated chemically homogeneous surfaces, with good optical properties but sometimes too rough to be imaged by a LPM. It is now necessary to fabricate a quite smooth surface with both luminescent and non-luminescent nanostructures or characterized by light-emitting systems of different chemical species (i.e., with different X-ray absorption edges). On such samples, using our SNOM head prototype and taking advantage of the energy tunability of SR, we could perform the X-ray absorption spectroscopy of single nanostructures discrminating among their chemical nature. Moreover, by taking the near-field optical image of the surface at different X-ray energies (before and after the absorption edge of a given chemical species), it would be possible to obtain a chemical map of the sample, with the lateral resolution of LPM. At the same time we could also record the topographical image of the surface.

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2. S. Larcheri, C. Armellini, F. Rocca, A. Kuzmin, R. Kalendarev, G. Dalba, R. Graziola, J.Purans, D. Pailharey and F. Jandard, **Optical Materials** *28 (2006), 864-867*