

A new tool for nanoscale X-ray absorption spectroscopy and element-specific SNOM microscopy

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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 microbeams 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.

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1. Introduction

The understanding of phenomena occurring in nanosystems strongly needs experimental techniques able to work at the nanoscale. A multi-modal approach based on the coupling of methods capable of providing chemical as well as structural information is a possible starting point to bring together the processing tools, characterization equipment and technical expertise needed to span these length scales.

For instance, the extremely high-lateral resolution of scanning probe microscopes (SPMs) makes them leading actors in all domains of nanoscience and nanotechnology. SPMs provide key information on surface morphology and allow a local characterization of a wide number of physical properties, with a resolution going down to the atomic scale

(Lahtonen et al., 2006; Staderman et al., 2003). Unfortunately, these tools suffer of a lack in chemical sensitivity.

On the other hand, X-ray absorption spectroscopy (XAS) probes the average chemical and structural properties around selected atoms, being able to determine chemical composition and state, bond lengths, coordination numbers and dynamical properties on the atomic scale (Tsuji et al., 2004). The main limitation of XAS is the lack of spatial resolution, the lateral being coincident with the dimensions of the X-ray beam and the in-depth being strongly dependent on the X-ray energy. Furthermore, the possibility of “touching” and mechanically interacting with samples of nanometric dimension is a feature that synchrotron radiation does not exhibit, despite its importance as characterization tool in the nanoworld.

Thus, SPM and XAS provide complementary information, and it appears extremely tempting to merge them in order to get a deeper insight in physical and chemical properties of materials at the nanoscale. Recently, by coupling STM and XAS methods and measuring the photo-induced current, an

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estimated spatial resolution of the chemical imaging less than 20 nm has been demonstrated on an array of square Ni dots, fabricated on a Au-coated Si(0 0 1) wafer by electron-beam lithography (Eguchi et al., 2006). Another approach, based on the electrostatic force microscopy coupling with XAS, has been used recently to study oxidation of a silicon surface with less than 1 nm spatial resolution (Ishii et al., 2007).

In this work, we present a novel technique developed within the EC FP6 “X-TIP” project that is based on this idea. The new instrumentation uses the optical fiber tip of a scanning near-field optical microscope (SNOM) to detect the X-ray excited optical luminescence (XEOL) of a sample irradiated with a synchrotron radiation microbeam. Thus, the XAS–SNOM head microscope can be seen as the natural extension of a microprobe instrument having chemical sensitivity and morphology recognition. The main advantage of this approach is that the lateral resolution is determined by the SNOM tip and not by the X-ray spot size.

The first results, obtained with the prototype instrumentation installed at ID03 beamline at the European Synchrotron Radiation Facility (ESRF; Grenoble, France), illustrate the possibility to obtain an element-specific contrast and to perform nanoscale-XAS experiments by detecting the Zn K and W L₃-absorption edges in pure ZnO and mixed ZnWO₄/ZnO thin films.

2. Experimental

Synchrotron radiation measurements were performed at the ESRF storage ring, operated at 6 GeV and 200 mA, using our XAS–SNOM prototype instrumentation. The ID03 beamline, equipped with a channel-cut Si(1 1 1) monochromator and Kirkpatrick–Baez (KB) focusing optics, was used as a microfocusing X-ray source. The monochromatic X-ray beam, scanning in the energy range from 9600 eV to 10,400 eV, was used to excite the XEOL signal across the Zn K-edge (at 9659 eV) and W L₃-edge (at 10,207 eV). The size of the microbeam at the sample was 5 μm × 5 μm. The X-ray flux (measured by a dedicated beam monitor, located at the exit of the KB system) at 9700 eV was 3.4×10^{12} photons/s.

The scheme of the XAS–SNOM prototype is shown in Fig. 1. The microscope operates in collection mode using a tapered optical fiber probe (NT-MDT) glued to an oscillating quartz tuning-fork. The tip aperture is 50–100 nm. The optical signal is collected in near-field condition (Bethe, 1944; De Serio et al., 2003), i.e. it comes out from the sample region under the tip having the depth less than the tip aperture. Shear-force feedback (Karrai and Grober, 1995) is employed to regulate the probe-sample distance and to record the topographic image of the sample surface. The absolute positioning of the tip and of the sample with respect to the X-ray beam is performed thanks to a six-independent-axis

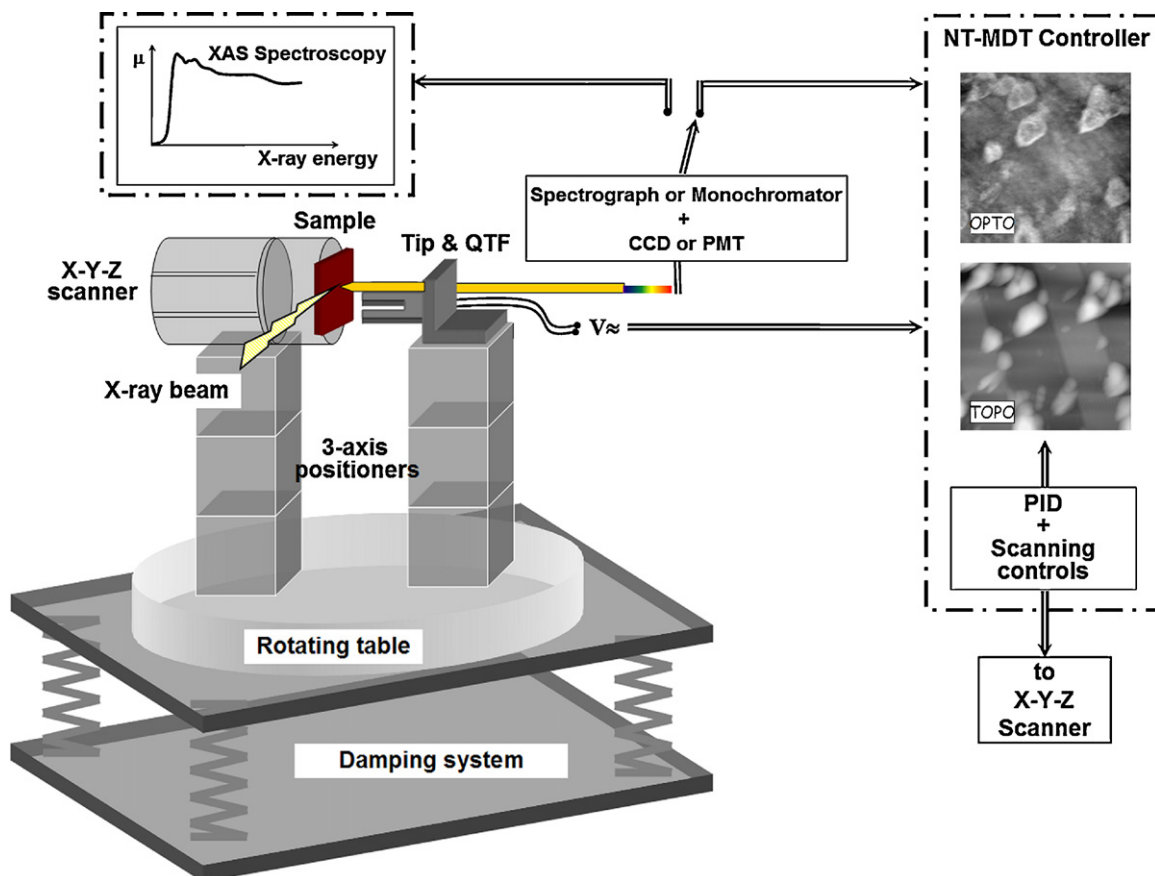


Fig. 1. Scheme of the XAS–SNOM microscope head and XEOL detection/analysis setup.

system. In order to collect the XEOL signal by means of the optical fiber tip, the imaging is carried out scanning the sample under the probe, while the tip is kept fixed with respect to the radiation beam. The microscope prototype is completed by a sturdy circular base to change the incidence angle of the X-rays on the sample and by a damping stage to attenuate the mechanical vibrations.

The voltage signal of the quartz tuning-fork and the XEOL signal collected by the fiber tip are monitored by the NT-MDT controller to record the topographic and optical images, respectively. Instead, the XEOL and XEOL–XAFS spectra are registered and displayed by another dedicated software, after undergoing a specific spectral analysis. The photon detection is carried out by means of a spectrograph/monochromator, coupled to a CCD camera for fast spectral analysis or to a photomultiplier for optical imaging and spectroscopic applications.

In a conventional laboratory environment the microscope prototype produces highly resolved topographic and optical images with a lateral resolution down to 100–200 nm. The topographic vertical resolution is about 2–3 nm and is limited by the noise of the piezo-scanner signal in the Z direction.

Pure ZnO and mixed ZnWO₄/ZnO thin films were deposited on a silicon substrate by dc magnetron co-sputtering technique from metallic zinc (99.9%) and tungsten (99.95%) targets, in pure argon and mixed argon(80%)–oxygen(20%) atmospheres, respectively, with subsequent annealing in air at 900 °C during 4 h. The films were characterized by X-ray diffraction (XRD), micro-Raman and atomic force microscopy (AFM). Both films are nanocrystalline with a broad distribution of grain sizes. The Raman spectrum of pure film shows vibration bands due to ZnO, while the one of mixed film is dominated by ZnWO₄ bands. Green photoluminescence was observed in both samples under X-ray excitation: this broadband emission peaks at ~530 nm in pure ZnO film, while originates from a superposition of two bands due to ZnO (~530 nm) and ZnWO₄ (~500 nm) phases in the mixed film.

Two types of experiments can be performed, at room temperature, using synchrotron radiation:

- (1) *Single-point nano-XAS*: the SNOM probe is placed in a point of interest over the sample surface and kept at the same position in near-field condition while the X-ray energy is tuned across an absorption edge (in the present case of Zn or W). A set of XEOL spectra is collected in the range of 300–800 nm, at increasing X-ray energy. The X-ray absorption near-edge structures (XANES) spectrum is obtained by plotting the XEOL intensity collected at a selected wavelength as a function of the X-ray energy (Dalba et al., 2000). The typical acquisition time for a single XANES spectrum is about 40 min.
- (2) *Element-specific profilometry*: the prototype operates in a conventional scanning mode, providing simultaneously the topographic and optical images of the surface. The optical image corresponds to the variation of the XEOL intensity, excited at a fixed X-ray energy and collected at a fixed (500 nm) wavelength. In order to obtain an element-specific contrast, different optical images are collected and compared by tuning the X-ray energy below and above the

Zn or W absorption edges. The acquisition time for collecting simultaneously at a single X-ray excitation energy the topographic and XEOL images (1024 × 1024 pixels, 18 μm × 18 μm) was about 2 h.

Due to the very high-photon density of the X-ray beam available at ID03, the tip material itself was luminescent under X-ray excitation, thus contributing to the background of the luminescence signal. To minimize this effect, the very apex of the tip was retracted as much as possible from the beam. At the same time, we did not monitor any damage of the sample or of the tip during subsequent measurements.

3. Results and discussion

An example of the single-point nano-XAS experiments is presented in Fig. 2 for pure ZnO and mixed ZnWO₄/ZnO thin film samples. The Zn K-edge XANES signal in pure ZnO film is similar to that found in polycrystalline ZnO (Larcheri et al., 2006) and shows fine structures well beyond the absorption edge. However, the first main peak at about 9666 eV has a noticeably higher intensity in the film than in polycrystalline ZnO.

In the mixed thin film, composed of two phases, ZnWO₄ and ZnO, one expects that the XANES signal measured at the W L₃-edge corresponds to the local environment around tungsten atoms in ZnWO₄ phase, whereas the Zn K-edge XANES represents a mixture of two signals, being due to zinc atoms located in ZnWO₄ and ZnO phases. The results in Fig. 2 are in agreement with this expectation. In fact, a comparison of the W L₃-edge XANES spectra (Fig. 2(b)) measured in near-field mode, with that obtained for polycrystalline ZnWO₄ in transmission mode (Kuzmin and Purans, 2001), indicates their great similarity. Both signals consist of the strong “white line” maximum at ~10,207 eV, related to the dipole-allowed

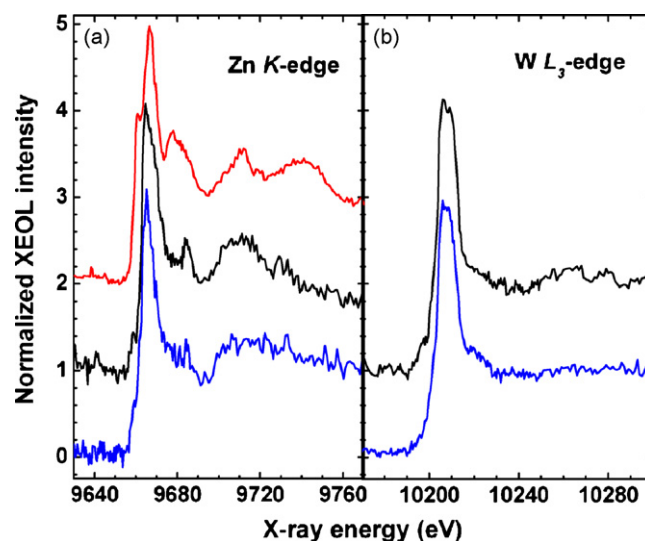


Fig. 2. Normalized XANES–XEOL spectra at (a) Zn K-edge and (b) W L₃-edge. Upper curve in (a) corresponds to a nanostructured ZnO thin film; other curves in (a) and (b) correspond to ZnWO₄/ZnO thin film. The XEOL signals were detected at 500 nm. The signals are up-shifted for clarity.

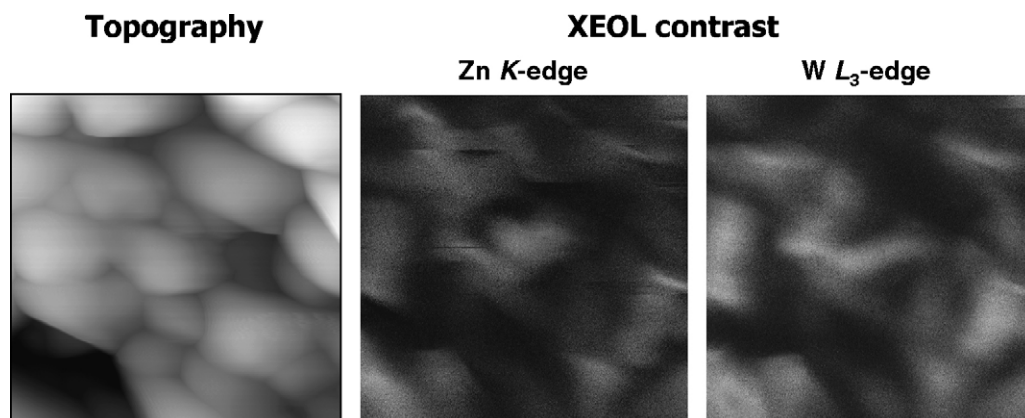


Fig. 3. Topography (left) and XEOL contrasts at the Zn K (center) and W L_3 -absorption edge (right) of a $ZnWO_4/ZnO$ thin film. The images size is $18 \mu\text{m} \times 18 \mu\text{m}$. The XEOL contrast image corresponds to the difference between two XEOL images measured above and below the correspondent absorption edge.

transition $2 p_{3/2}(W) \rightarrow 5d(W)$, and of a fine structure above it, due to the excited photoelectron scattering by the surrounding atoms. In the case of the Zn K-edge (Fig. 2(a)), the XANES spectrum corresponds to a mixture of pure $ZnWO_4$ and ZnO chemical phases (Larcheri et al., 2006; Pailharey et al., 2007).

These results show that the X-ray absorption spectra at the Zn K-edge and W L_3 -edge can be recorded through the SNOM probe in near-field condition with a quite high signal-to-noise ratio. To our knowledge, this is the first time that near-field XANES–XEOL spectra are recorded by means of a SNOM microscope integrated on a synchrotron radiation facility. The reproducibility of all acquired spectra has been checked out, obtaining positive results in terms of system and X-ray beam stability. As an example of the quality of data, we present a few XANES spectra collected at the Zn K and W L_3 -edges in Fig. 2.

In the second kind of experiments, topographic and XEOL-optical images were recorded simultaneously for the mixed $ZnWO_4/ZnO$ thin film at four X-ray energies, respectively below and above the Zn K and W L_3 -edges. The optical luminescence signal in this film originates both from the oxyanionic WO_6 groups of $ZnWO_4$ and from defects in ZnO. The XEOL contrast images were calculated as the difference between the two optical images obtained below and above each absorption edge. An example of the topographic image and XEOL contrast images is reported in Fig. 3. From the characterization by XRD, micro-Raman and AFM, we know that this film is composed of nanocrystalline $ZnWO_4$ and ZnO, finely mixed within the grains visible in the topographic image (Fig. 3). The bright features in the optical contrast images at the Zn K-edge and at the W L_3 -edge correspond to the distribution of those luminescent centers that are directly related to the X-ray absorption by zinc and tungsten atoms, respectively. At the same time, the dark points correspond to places where the XEOL signal does not change across the X-ray absorption edge.

Thus, the combined XAS–SNOM technique extends the capabilities of conventional SNOM microscopy, allowing a chemically sensitive mapping of the sample surface with the spatial resolution offered by the sub-wavelength hole of the optical fiber probe. By repeating this kind of measurements, the XAS–SNOM detection setup has shown a good sensitivity to small variations of the optical signal, both by scanning the

X-ray energy across different absorption edges and by probing surfaces characterized by different chemical, morphological and optical properties. Moreover, the microscope has been proved capable of high imaging reproducibility, confirming that the observed features are actually related to the topographical and near-field optical properties of the sample.

4. Conclusions

In this paper we have presented a novel instrumentation that combines X-ray absorption spectroscopy using synchrotron radiation microbeams with scanning near-field optical microscopy in a unique characterization tool. Our XAS–SNOM microscope collects the X-ray excited optical luminescence in near-field conditions using a tapered optical fiber probe, glued to an oscillating quartz tuning-fork.

The device, specifically manufactured to operate in the harsh synchrotron radiation environment, has been successfully installed and integrated with the ESRF-ID03 beamline software control and data acquisition system. By using a custom-tailored anti-vibration system, our setup commonly achieves the lateral resolution of about 100–200 nm and the vertical resolution of about 3 nm.

The capabilities of the combined XAS–SNOM technique have been explored performing two types of experiments, on pure ZnO and mixed $ZnWO_4/ZnO$ nanostructured thin films. First, we have recorded high quality XANES–XEOL spectra, using synchrotron radiation as exciting source and collecting the XEOL signal in near-field condition. This opens the possibility to study 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. Second, we have carried out experiments of element-specific profilometry, in which conventional SNOM microscopy is enriched by sensitivity to chemical elements. By comparing different optical images, we were able to obtain maps of both Zn and W distribution.

This research project holds out promise for future developments not only of the combined XAS–SNOM technique but, more in general, of the joint use of scanning

probe microscopies and X-ray absorption techniques. The feasibility study performed so far has demonstrated that an approach based on local tip detection of X-ray absorption yields can provide an invaluable tool to obtain fundamental information on structural, electronic and optical properties of matter at the nanoscale.

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