EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** EXAFS characterization of substoichiometric tungsten oxide films fabricated by RF-sputtering for plasmonic-based nanodevices	**Experiment number**: MA-5672
Beamline: BM08	**Date of experiment**: from: 03 March 2023 to: 06 March 2023	**Date of report**: 1st June 2023
Shifts: 9	**Local contact(s)**: Francesco D'ACAPITO	*Received at ESRF:*

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Report:

Scientists on the beamline were Silvia M. Pietralunga, Hao Chen and Francesco D'Acapito.

We characterized sub-stoichiometric and amorphous WO_{3-x} compact thin films, synthesized by non-reactive radiofrequency (RF) sputtering from WO_3 targets, according to Ref. [1]. The stoichiometry of as-deposited films had been modified by subsquent 8-hours thermal annealing in different conditions and atmospheres (dry air, N_2, and vacuum). Annealing temperatures had been chosen below and above crystallization thresholds, according to the atmosphere and the expected stoichiometry. Crystallization was checked at home institutions by XRD and SEM imging. Films were crystallized at 400 °C if in air and at 650 °C if either in N_2 or in vacuum. Specimens of fully oxidized samples, crystallized in air and e-beam irradiated for stoichiometry reduction, were also measured.

The goal of EXAFS investigation was to highlight differences in the local structure and coordination of differently prepared WO_{3-x} films. Measurements were performed at W-L3 edge (10207 eV), with the energy ranging from 10006 eV to 11000 eV, thus covering both XANES and EXAFS. Data was collected at room temperature in low vacuum and at low temperature (80 Kelvin) in high vacuum. Energy dependence of absorption coefficient $\mu(E)$ was recorded in fluorescence mode, $\mu(E) = I_f/I_0$, where I_0 is the X-ray beam intensity before sample and I_f is the intensity of fluorescence after sample. In order to minimize the contribution from the substrate, the focused X-ray beam was at grazing incidence (45 degrees). The interpretation of data is supported by characterizions performed at home institutions, including morphological, optical, structural, chemical and electrical properties.

Collected data was cleaned from background and normalized by Athena program of Demeter software package, so that the data become independent of details of measuring configuration or detector setup. The cleaned data expresses energy-dependent absorption coefficient as $\chi(E) = [\mu(E) - \mu_0(E)]/\Delta\mu_0(E)$, where $\mu_0(E)$ represents background absorption and $\Delta\mu_0(E)$ represents absorption jump at edge energy. In Figure 1 the top

panel shows the EXAFS spectra of WO_{3-x} thin films before and after annealing in different atomspheres, plotted in k space weighted by k^2. It shows spectral differences between as-deposited (amorphous) thin film and annealed ones (crystallized). The reason that causes this difference may be two-fold. The similarity of EXAFS spectra between crystallized samples annealed in air (monoclinic) and in N_2 (triclinic) suggests that the first reason of difference from the as-deposited sample might be the reorganization of structure into an ordered distribution of atoms. From this similarity we may also infer that small stoichiometric differences may occur between the two crystallized samples but under the sensitivity of EXAFS. Actually, from optical and electrical measurements it is expected that annealing in air leads to more stoichiometric samples. Differences of the order of $x = 0.1$ in WO_{3-x} can already induce significant changes in optical and electrical properties and yet still be not recorded by EXAFS. But if the compositional difference increases, as is the case for the sample annealed in vacuum, where structural measurements tell that WO_2 forms, the EXAFS plot is clearly different. This large compositional change makes up the second contribution of previously mentioned difference.

Regarding the e-beam irradiated samples, which are expected to be chemically reduced but up to an unknown degree, EXAFS spectra are shown in Figure 2 and look quite similar to non-irradiated sample. We deem it to be under EXAFS sensitivity for the stoichiometric changes by the applied e-beam irradiation dose, so that nothing significant can be inferred from the present results, concerning possible variations in local coordination induced by e-beam irradiation. More effettive e-beam treatments should be put in place, to address EXAFS analysis in a further experimental session.

Fourier transformed radial distance distribution is depicted in the bottom panels of Figure 1 and Figure 2. Fourier transform range was 3 $Å^{-1}$~10.8 $Å^{-1}$, but higher wavenumbers are not included because of poor data detection, due to unknown reasons. In the first-shell (1 Å ~ 2 Å) two main peaks are evident, meaning two main W-O bond distances, and their relative magnitude is modified in dependence of annealing conditions.

EXAFS fitting was performed using Artemis software. The total coordination number in the first shell is set to $N_{total} = 6$ and two different paths are used, respectively representing short and long W-O distances. Fitting result shows that the short W-O distance is dominant in as-deposited sample (N = 4 for short W-O distance and N = 2 for long W-O distance) and this remains after annealing in air and in N_2. Instead, by annealing in vacuum, the preference is switched to long W-O distance (N = 2 for short W-O distance and N = 4 for long W-O distance). Fitting over the extended shells has proven to be quite difficult and work is still in progress.

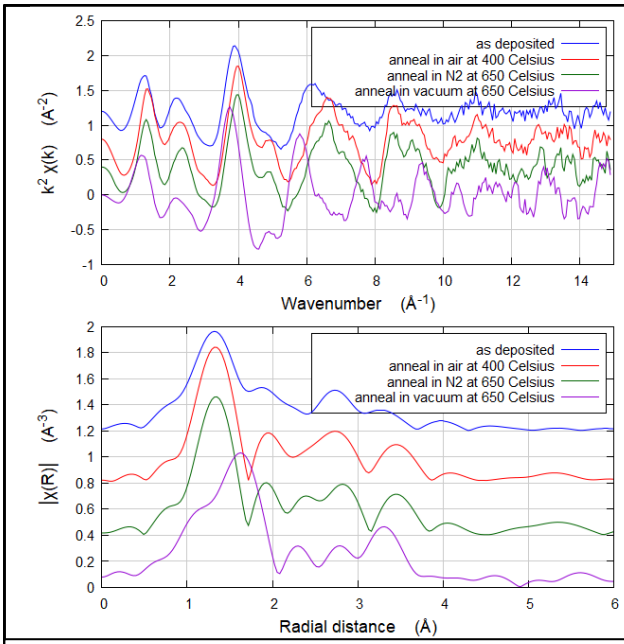

Figure 1. EXAFS spectra of differently post treated WO_{3-x} thin films in k space (top) and the corresponding Fourier transformed radial distance distribution (bottom).

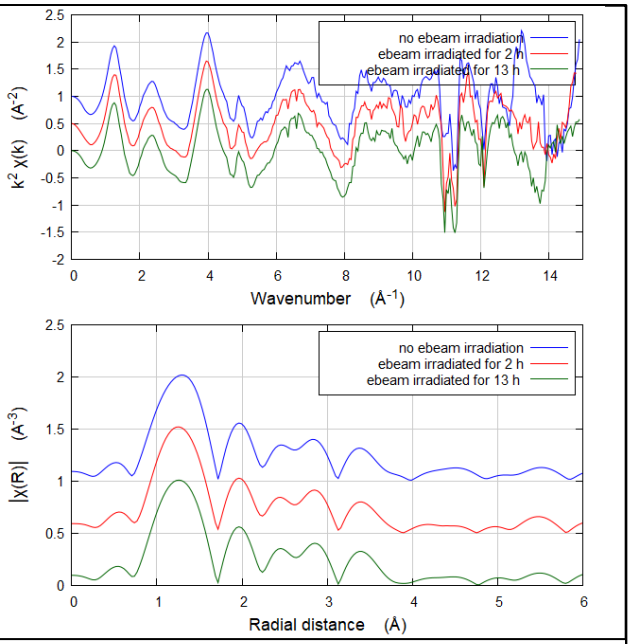

Figure 2. EXAFS spectra of ebeam irradiated WO_{3-x} thin films in k space (top) and the corresponding Fourier transformed radial distance distribution (bottom).

[1] H. Chen et al., "Tungsten oxide films by radio-frequency magnetron sputtering for near-infrared photonics," Optical Materials: X 12 (2021) 100093.