EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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: Characterization of ceria/aluminum oxide and ceria/metallic contacts interfaces of a novel nanostructured resistance-based hydrogen sensor for operation at room temperature**	**Experiment number**: 25-02-980
Beamline: BM25 Spline	**Date of experiment**: from: 04 May 2021 at 08:00 to: 10 May 2021 at 08:00	**Date of report**: 12.07.2021 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Juan Rubio Zuazo	

Names and affiliations of applicants (* indicates experimentalists):

* Dr. Carlos Morales Sanchez

Prof. Dr. Jan Ingo Flege

* Emilia Pozarowska

* Ali Mahmoodinezhad

The experiment was carried out in remote mode.

Report:

Experimental *(the experiment was performed in remote mode due to Covid-19 restrictions):*

The experiment was performed at the Spanish CRG BM25 Spline beamline (Spanish CRG beamtime assignation). Ceria (CeO_x) films (10 nm) grown on Al_2O_3(10 nm)/Si and SiO_2 substrates were studied by HAXPES and SXRD after different thermal treatments to characterize chemical and structural changes on thin films and follow, in particular, the possible interaction between film and substrate at the interface region. Precisely, the investigation focused on the possible development and fixation of Ce^{3+} states –forming cerium aluminate, $CeAlO_3$- after different annealing processes: under ultra-high-vacuum (UHV) conditions and under H_2 atmosphere ($1.0 \cdot 10^{-5}$ mbar). After each of these treatments, ceria ultra-thin films were re-oxidized by exposing them to ambient conditions (room atmosphere, room temperature (RT)). The CeO_x/SiO_2 sample was measured for comparison purposes. In order to enhance the difference between surface and interface regions, cerium Ce 3d and Ce $2p_{3/2}$ core levels were measured above and below the total reflection (TR) angle. The following table summarizes the experimental plan carried out:

	General: hν = 10 keV & λ = 1.23984 Å		
Sample	**Treatment and measurements**	**Sample**	**Treatment and measurements**
$CeO_x/Al_2O_3/Si$	SXRD & HAXPES: Ce 3d, O 1s, Al 1s, Ce2p • As inserted • Annealing at 500 °C, UHV, 1 hour • Re-oxidized: exposed to air, RT, 20 min. • Annealed at 500 °C, 10^{-5} mbar, 1 hour • Re-oxidized: exposed to air, RT, 20 min. • Annealed at 500 °C, 10^{-5} mbar, 1 hour • Re-oxidized: exposed to air, RT, 20 min. • Annealed at 500 °C, 10^{-5} mbar, 30 min • Re-oxidized: exposed to air, RT, 20 min.	CeO_x/SiO_2 $CeO_x/Al_2O_3/Si$ and CeO_x/SiO_2 *(simultaneusly treatment)*	SXRD HAXPES: Ce 3d, O 1s, Al 1s, Ce2p • As inserted SXRD HAXPES: Ce 3d, O 1s, Al 1s, Ce2p • Annealing at 500 °C, UHV, 1 hour

Results

HAXPES measurements show chemical changes under different reduction-oxidation cycles. On the one hand, Figure 1 shows how the A 1s peak slightly broadens after each reduction process applied on $CeO_x/Al_2O_3/Si$ films. According to the literature, the expected development of aluminate species ($CeAlO_3$) at the interface would translate to a new contribution at lower binding energies than the Al_2O_3 peak, thus explaining the observed widening. On the other hand, the ceria film shows a change in the Ce^{3+}/Ce^{4+} ratio after the different reduction/re-oxidation processes ($CeO_x/Al_2O_3/Si$). Figure 1 a and b shows the Ce 3d and Ce 2p (black and blue, interface and surface sensitive measurements, respectively). As it can be inferred from both measurements, the as-inserted sample is slightly reduced (especially at the surface region). However, after the first annealing process under UHV conditions, the Ce^{3+}/Ce^{4+} ratio increases, showing a significant reduction of the film within all its thickness. As indicated above, simultaneously, the Al 1s core level evolution indicates the possible development of aluminate species, as expected. The sample was re-oxidized after exposed to room conditions for several minutes, recovering its initial oxidation state. Surprisingly, after the second reduction process consisting of annealing under H_2 atmosphare, the ceria film does not reduce as for the UHV case, but preserves a very similar Ce^{3+}/Ce^{4+} ratio from the re-oxidized sample. This result was not expected, as ceria reduction-oxidation processes are well-known to be reversible on thicker samples, actually used for oxygen storage. This reduction/oxidation cycle using H_2 was repeated several times, leading to identical results. Besides, a CeO_x/SiO_2 sample was used for comparison purposes. Simultaneously with the previous sample, the same annealing under UHV conditions and subsequent re-oxidation processes were repeated (not shown here). In this case, the $CeO_x/Al_2O_3/Si$ keeps on the same behaviour, while the CeO_x/SiO_2 sample clearly reduces and re-oxidizes. Therefore, preliminary results indicate that the ceria/alumina interaction prevents the reversibility of changes on the Ce^{3+}/Ce^{4+} ratio. SXRD measurements do not clarify the appearance of new ordered phases.

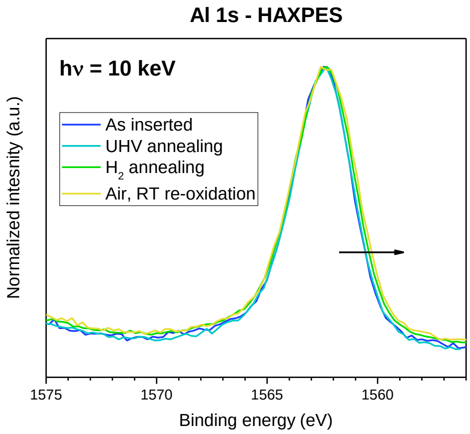

Figure 1. Normalized Al 1s spectra after different reduction and re-oxidation processes performed on $CeO_x/Al_2O_3/Si$ sample

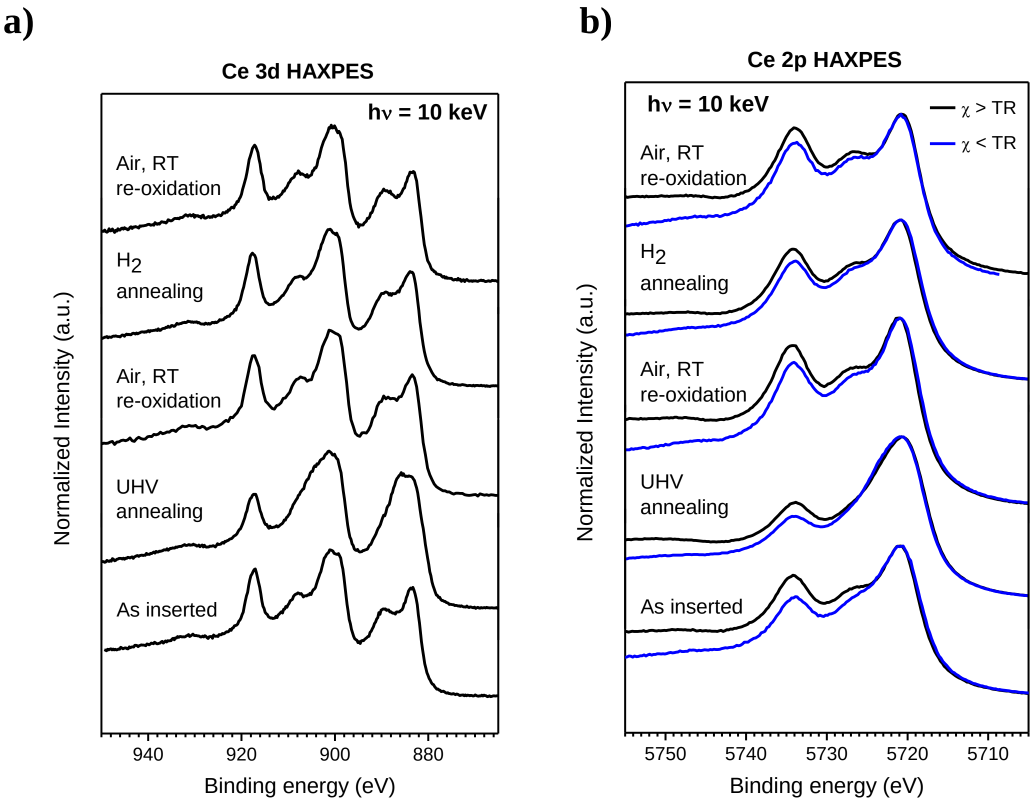

Figure 2. a) Ce 3d and Ce 2p spectra after different reduction and re-oxidation processes performed on $CeO_x/Al_2O_3/Si$ sample. In black and blue, respectively, interface (taken at >TR conditions) and surface (taken at <TR conditions) cond senstive measurements, respectively