



	<b>Experiment title:</b> Structural modifications induced by reduction in cerium oxide ultrathin films	<b>Experiment number:</b> HC 1848
<b>Beamline:</b> BM08	<b>Date of experiment:</b> from: 15.07.2015 to: 20.07.2015	<b>Date of report:</b> 22/02/2016
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## Report:

The aim of the experiment was to study the structural modifications which occur during reduction of cerium oxide ultrathin films supported on Pt(111). The investigated topic is important in view of obtaining a better understanding of the reducibility of ceria and related oxides. The experiment is based on previous studies [1-2], which showed that thermal reduction in vacuum induces specific surface reconstructions in ultrathin films, and on a previous experiment performed at ID26 (HC-1267), which demonstrated a surprisingly high reducibility for the same systems.

To have more detailed information on the structure of the reduced phase, we performed XAS measurements at the Ce L<sub>3</sub>-edge, at progressive degrees of reduction. Three cerium oxide films were grown in our laboratories by reactive MBE on a Pt(111) substrate. Two of the samples, a 2 ML and a 10 ML thick film, were annealed in O<sub>2</sub> after the growth, to induce a regular morphology and a good epitaxial quality [1]. A third sample with 2 ML thickness was prepared without the post-growth annealing treatment and it showed a surface with grains of nanometric size with a random orientation and a high density of undercoordinated sites [1]. For comparison, we also measured a film made of CeO<sub>2</sub> nanoparticles (NP), grown by magnetron sputtering and inert gas aggregation on a Si/SiO<sub>x</sub> substrate [3]. The average NP diameter was 9 nm. The samples were carried to the ESRF in non-reactive atmosphere. Moreover, we measured two reference samples: a CeO<sub>2</sub> (Ce<sup>4+</sup> reference) powdered sample, measured in the transmission mode, and a cerium silicate (Ce<sup>3+</sup> reference) film, measured in the fluorescence yield mode.

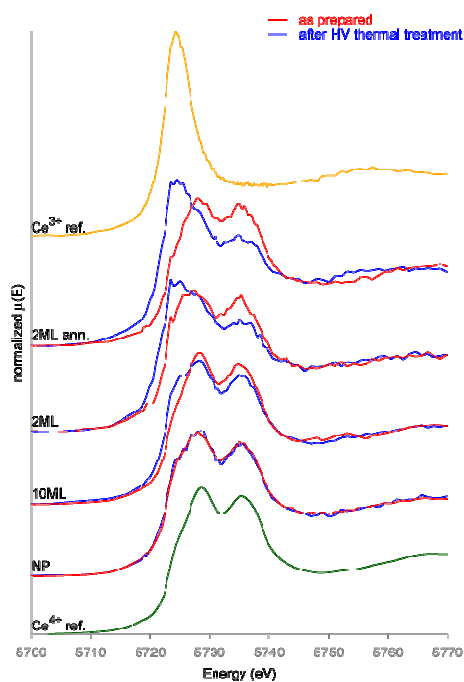
The cerium oxide films were mounted in a high-temperature furnace (Micro-Tomo from the Sample Environment Support Department), which was installed in the BM08 acquisition chamber and used to apply *in-situ* thermal treatments to the sample in high vacuum (HV) conditions. The samples were measured in the fluorescence yield mode using a single element detector, the solid angle of detection being limited by the furnace window. This limitation, together with the low thickness of the ceria films, made the measurements very challenging. Ce L<sub>3</sub>-edge spectra in the near and extended energy range were acquired before and after a reducing thermal treatment in HV at 750°C.

The XANES spectra show significant changes after the thermal treatment only in the 2 ML samples, while the 10 ML sample and the NP sample spectra are not relevantly modified (Fig.1). This evidence is consistent with the hypothesis of cerium oxide reduction involving only a limited sample thickness.

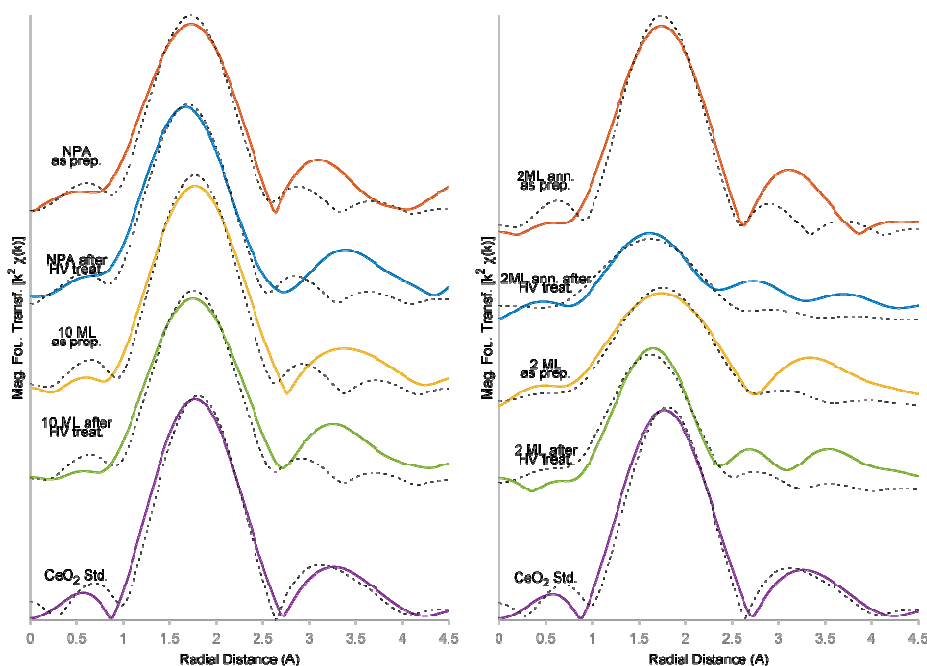
The quality of the spectra in the full EXAFS range was acceptable up to  $k=6 \text{ \AA}^{-1}$  for the 2 ML and NP samples, therefore for consistency we used the  $k=2.5-6.0 \text{ \AA}^{-1}$  range for all samples spectra. The data analysis was limited to the first coordination shell and it was performed using the theoretical scattering functions generated by the FEFF program, with the Ce-O distances, the Debye-Waller factors and energy origin shift as free fitting parameters. The  $S_0^2$  value was kept fixed to the one obtained from the fitting of the reference  $\text{CeO}_2$  sample. Fig.2 shows the magnitude of the Fourier transforms of  $k^2$ -weighted  $\chi(k)$  and the corresponding fittings for the four samples before and after the HV reducing treatment. The spectra and the fitting of the  $\text{CeO}_2$  reference sample in the same  $k$  range are also reported for comparison.

The results obtained from the fittings are here summarized. As already pointed out in our previous work [4], in epitaxial films, the 10 ML  $\text{CeO}_2$  film has a few percent larger Ce-O distance compared to the 2 ML film, ascribed to the relaxation of the epitaxial compression. Consistently, the non epitaxial film shows a Ce-O average distance comparable to the 10 ML film. Moreover, we observed a higher value for the apparent Debye-Waller factor obtained for the granular 2 ML film compared to the 2 ML epitaxial film, which is probably an indication of the worse local structural order of the granular sample. After the reducing treatment, both the 10 ML film and the NP sample do not show significant modifications of the Ce-O distances, consistent with the very low global  $\text{Ce}^{3+}$  concentration induced in these samples by the treatment and with the spectra being dominated by the  $\text{CeO}_2$  phase. In the 2 ML samples, instead, a small contraction of the Ce-O distance after reduction is observed as a consequence of the HV thermal treatment. This is consistent with the formation of the most stable A-type  $\text{Ce}_2\text{O}_3$  phase at high reduction degrees.

Finally, we note that the quality of the fitting for the 2 ML samples after the thermal treatment in HV is slightly improved by introducing a Ce-Pt scattering path, which possibly indicates the formation of an interfacial alloyed phase with a Ce-Pt distance compatible with the one in the  $\text{CePt}_5$  alloy, although, given the data quality this indication is not fully reliable and it deserves further investigation.



**Fig.1:** Ce  $L_3$ -edge XANES spectra of the four samples before and after the HV thermal treatments. Spectra from  $\text{CeO}_2$  and cerium silicate reference samples are also shown.



**Fig.2:** Magnitude of the Fourier transform of the  $k^2$ -weighted Ce  $L_3$ -edge  $\chi(k)$  (solid lines) and first-shell fits (dashed lines) of the four samples before and after the HV thermal treatments. Spectra from  $\text{CeO}_2$  reference sample in the same  $k$  range used for the different samples are also reported.

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