ESRF

Experiment title:
Modification of the electronic properties of cerium oxide films induced by controlled reduction/oxidation

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Local contact(s):
Jean-Daniel Cafun

Names and affiliations of applicants (* indicates experimentalists):
Paola Luches*[1], Lucia Amidani*[2], Federico Boscherini*[2], Sergio Valeri[1,3]
[1]Centro S3, Istituto Nanoscienze, Consiglio Nazionale delle Ricerche, Modena, Italy
[2]Dipartimento di Fisica e Astronomia, Università di Bologna, Bologna, Italy
[3]Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, Modena, Italy

Report:

In this experiment we investigated the electronic structure of cerium oxide ultrathin films by resonant inelastic X-ray scattering (RIXS) at the Ce L_3 edge, during reduction and oxidation processes. The aim of the experiment was to clarify the mechanisms responsible for the peculiar properties of cerium oxide, i.e. its ability to store, transport and release oxygen depending on the ambient conditions.

The experiment was based on some of our previous studies on cerium oxide films, which showed that the concentration of Ce^{3+} species can be reversibly modified by thermal treatments in vacuum/oxygen [1, 2]. The samples for the present experiment were grown in our laboratories by reactive deposition of cerium in oxygen atmosphere on a Pt(111) substrate, and they were brought to the ESRF in non-reactive atmosphere. Three cerium oxide films differing in structure, morphology and thickness were investigated. Two of the samples were epitaxial films, with 2 and 10 ML thickness, treated at 1040 K in oxygen atmosphere ($P_{O_2}=1\times10^{-7}$ mbar) after the growth to optimize their stoichiometry, morphology and crystal quality. For comparison we also measured an as-deposited cerium oxide film of 2 ML thickness, showing a nanostructured surface morphology. The samples were mounted in a high-temperature furnace to apply *in-situ* thermal treatments to the sample in reducing ($P < 10^{-7}$ mbar) and oxidizing ($P_{O_2}=1\times10^{-4}$ mbar) ambient. Each sample was first treated by a reducing heating cycle in vacuum (from RT to 1020 K and back to RT) and subsequently by an oxidizing heating cycle in O_2 (from RT to 1020 K and back to RT).

High-Energy Resolution Fluorescence Detected (HERFD) XANES measurements were performed by scanning the incident photon energy around the Ce L_3 edge and setting the emitted photon spectrometer at the energy of the $L_{\alpha1}$ fluorescence line ($3d_{5/2}$-$2p_{3/2}$ transition). From the analysis of the post-edge region we obtained information on the evolution of the 5d band, while the pre-edge region gave information on the modifications of the 4f electronic structure during reduction/oxidation processes. The data were acquired at specific temperatures (RT, 520 K, 770 K, 1020 K and RT) during the heating cycle in vacuum and in O_2. Two-dimensional RIXS maps were also acquired before the thermal treatments and after the reducing and oxydizing cycles, to obtain additional information on the evolution of the occupancy of the 4f states.

Fig.1 reports the HERFD-XANES spectra and the details of the pre-edge region of the 2 ML and 10 ML epitaxial samples during the thermal cycles in vacuum and O_2. Due to space limitations we omit the description of the spectra acquired on the 2 ML nanostructured film. The modifications of the shape of the spectra of the 2 ML epitaxial sample, both in the pre- and post-edge regions are very significant. By comparing the measured spectra with the ones of standard samples containing Ce in the nominally 4+ and 3+ oxidation states [3], it is evident that the shape of the 2 ML spectrum at RT is very similar to the Ce^{4+}

standard sample; it progressively evolves with T resembling the Ce^{3+} standard at 1020 K in vacuum and it gradually goes back to the original Ce^{4+} shape during the thermal treatment in oxygen. The 10 ML sample spectra instead show only minor changes during the thermal cycles, consistent with the evidence that reduction takes place mainly in the uppermost surface layers [2]. Each spectrum in the full XANES region and in the pre-edge region was fitted by a linear combination of the spectra of the 2 ML sample at 1020 K in vacuum and of the 10 ML sample at 1020 K in O_2, which represent the most significantly reduced and oxidized samples, respectively. The evolution of the Ce^{3+} concentration, i.e. of the relative weight of the Ce^{3+}-related component in the fitting, during the thermal cycles in vacuum and in O_2 for the two samples is shown in fig.2. This analysis shows that the evolution of the main features in the spectra, related to 2p-5d transistions, during reduction is accompained by a modification of the pre-edge-related features, due to dipole forbidden 2p-4f transitions. We note however that the thermal broadening of the spectral features induces some uncertainties in the fitting results.

Two RIXS maps of the pre-edge region for the 2 ML and 10 ML films before and after the reducing thermal treatment are shown in Fig.3. The differences in the shape, position and number of the pre-edge peaks after reduction reflect the different occupancy of 4f levels. The oxidized samples show a single pre-edge peak, while after reduction a second peak appears. It is noteworthy that the 10 ML mildly reduced film shows a significantly modified 4f configuration, with two pre-edge peaks in the same position as in the reduced and oxidized 2 ML film.

In summary, from the data analysis, combined with in-house results on the morphology and the structure of the samples, we can draw the following conclusions: i) the reducibility of the 2 ML film is higher than the one of the 10 ML film, due to the influence of reduced dimensionality and to the proximity of the substrate; ii) the formation of oxygen vacancies in our samples involves a progressive filling of localized Ce 4f states. These results are described in a forthcoming paper [4].

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[4] G. Gasperi, P. Luches, L. Amidani, F. Benedetti, F. Boscherini, S. Valeri, submitted.

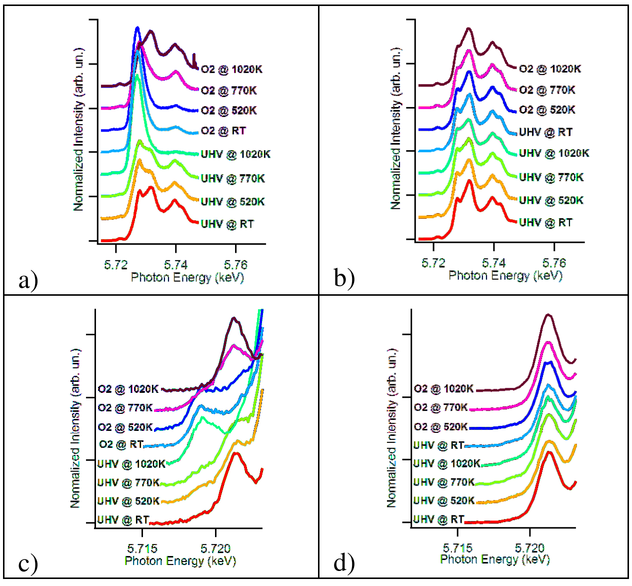

Fig.1: Spectra measured during thermal cycles in vacuum and in O_2 atmosphere: (a) XANES and (c) pre-edge spectra of 2 ML film, (b) XANES and (d) pre-edge spectra of 10 ML film.

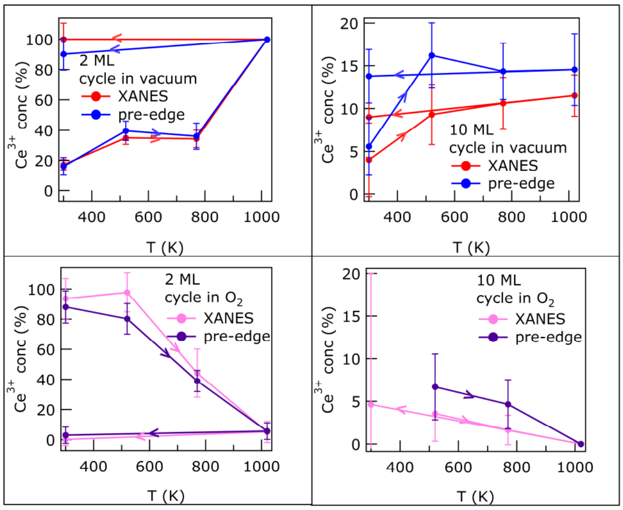

Fig.2: Evolution of the Ce^{3+} concentration in the 2 ML and 10 ML epitaxial films during thermal cycles in vacuum and in O_2. The Ce^{3+} concentration values were obtained by fitting the spectra in the full XANES range and in the pre-edge range by a linear combination of the spectra measured on the most significantly reduced and most significantly oxidized samples.

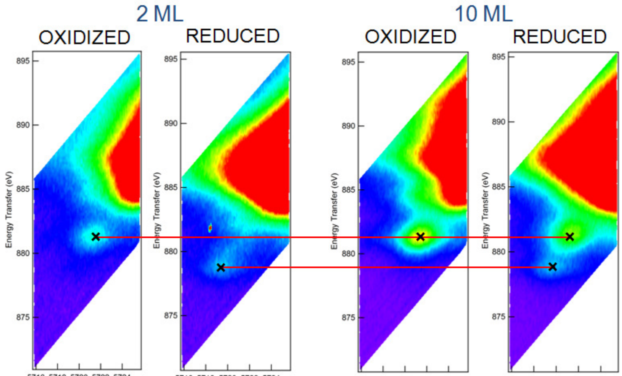

Fig.3: RIXS two-dimensional maps of the pre-edge region for the 2 and 10 ML film before and after the reduction process (i.e. thermal cycle in vacuum), measured at RT. The pre-edge peaks are evidenced by the black crosses. The differences in the shape, position and number of pre-edge peaks after reduction reflect the different occupancy of 4f levels. It is noteworthy that the 10 ML mildly reduced film shows a significantly modified 4f configuration, with two pre-edge peaks in the same position as the 2 ML oxidized and reduced films.